SOUTHERN CALIFORNIA AIR QUALITY STUDY QUALITY ASSURANCE PROGRAM

ENSR Document No. 1200-004-001 November 1989

Prepared for

CALIFORNIA AIR RESOURCES BOARD ARB Contract No. A6-122-32

Prepared by

John Collins Ensr Consulting and Engineering 1220 Avenida Acaso Camarillo, California 93010

and

Eric Fujita
Research Division
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

,			

ABSTRACT

The methods and results of the Quality Assurance Program for the Southern California Air Quality Study (SCAQS) are described. The program included system audits by ENSR Consulting and Engineering, performance audits by the California Air Resources Board (ARB) and the South Coast Air Quality Management District (SCAQMD), and several laboratory intercomparison studies coordinated by ARB.

System audits included review of standard operational and quality control procedures submitted by all study participants, onsite system audits of AeroVironment (AV) for the SCAQS sampler, Environmental Monitoring Services, Inc. (EMSI) for ions and mass, Environmental Protection Agency (EPA) for elemental composition and speciated hydrocarbons, SCAQMD for routine continuous gases, Tracer Technologies for tracers studies, Sonoma Technology, Inc. (STI) and University of Washington (UW) for airborne air quality and meteorological measurements, and T&B Systems for upper air soundings.

Continuous CO, SO₂, O₃, NO_x, and total hydrocarbons (THC) analyzers operated by the ARB at Long Beach, by General Motors at Claremont, by SCAQMD at Los Angeles - North Main, and by STI and UW aboard the aircrafts were audited during the summer field study. ENSR Consulting and Engineering conducted system audits for all measurements to review operational and quality control procedures and provided overall management of the quality assurance program. Performance audits of continuous gas analyzers and ion analysis were conducted by ARB, and audits of the SCAQS sampler flow rates were conducted by the SCAQMD. Additionally, intercomparison studies were coordinated by the ARB for elemental analysis, speciated hydrocarbons, light absorption and peroxyacetyl nitrate.

ACKNOWLEDGMENTS

We wish to thank the many participants who cooperated to improve and quantify the quality of measurements made during SCAQS. Particular thanks go to Bob Effa of the ARB Quality Assurance Section, whose teams conducted performance audits for continuous gas analyzers and meteorological instruments, and to Bill Bope and Sandy Ryan of the South Coast Air Quality Management District, whose teams conducted performance audits for sampler flow rate and for nephelometers. Dr. Richard Countess of C-E Environmental, Inc., Barbara Wright of ENSR, and Dr. Stanislaw Piorek of Columbia Scientific Industries provided assistance with the performance audits for ion chemistry. We especially thank the following individuals for their participation in the various comparison Dr. Bob Kellogg of NSI Technology Services, Inc.; Dr. John Cooper of NEA, Inc.; Dr. Bill Davis of the California Air Resources Board; Dr. Tom Cahill of the University of California, Davis; Drs. Ken Knapp, Len Stockburger and Bill Lonneman of the EPA; Dr. Rei Rasmussen of the Oregon Graduate Center; Dr. Hal Westberg of the University of Washington; Dr. Ray Weiss of Radiance Research; and Dr. Daniel Grosjean and Ed Williams of DGA, Inc. Finally, we wish to acknowledge the suggestions and assistance of Dr. Susanne Hering of Sonoma Technology, Inc. This project was funded by the Air Resource Board.

CONTENTS

1.	SUMMAR	Y	1-1
	1.1	SCAQS Quality Assurance Program	1-1
	1.2	Preliminary Audits	1-3
	1.3	Field Audits	1-4
	1.4	Special Studies and Intercomparisons	1-4
	1.5	Results of the Quality Assurance Program	1-4
	1.6	Recommendations	1-7
2.	RECOMM	ENDATIONS	2-1
3.	INTROD	OUCTION	3-1
4.	PRELIM	INARY AUDITS	4-1
	4.1	Hydrocarbon Speciation	4-2
	4.2	XRF Analysis	4-3
	4.3	Criteria Pollutants and Meteorology	4-3
	4.4	Perfluorocarbon Tracer Study	4-4
	4.5	SCAQS Sampler and SCAQS Sampler Ion Chemistry	4-4
5.	FIELD	AUDITS	5-1
	5.1	Field System Audits	5-1
	5.2	Flow Rate Performance Audits	5-3
	5.3	Nephelometer Audits	5-13
	5.4	Continuous Gas Analyzer Audits	5-13
	5.5	Meteorological Audits	5-19
6.	SPECIA	AL STUDIES AND INTERCOMPARISONS	6-1
	6.1	Nitrogen and Carbonaceous Species Methods	
		Comparison Studies	6-1
	6.2	Precision Test of SCAQS Sampler	6-2
	6.3	SCAQS Comparison Studies	6-3
		6.3.1 Elemental Analysis	6-3
		6.3.2 Speciated Hydrocarbons	6-10
		6.3.3 Light Absorption	6-13
		6.3.4 Peroxyacetyl Nitrate	6-16
7.	MEASUE	REMENT ACCURACY AND PRECISION	7-1
8.	REFERI	ENCES	8-1
9.	GLOSS	ARY	9-1

CONTENTS

(Cont'd)

APPENDIX A - BACKUP DATA FOR SCAQS SAMPLER ION CHEMISTRY AUDITS

- CSI Report
- C-E's Ion Chemistry Comparison From SCAQS Sampler
 Side-by-Side Testing

APPENDIX B - ARB QUALITY ASSURANCE SECTION: AIR QUALITY AND METEOROLOGICAL AUDIT REPORT

APPENDIX C - DATA FROM INTERCOMPARISON OF SCAQS FILTER ELEMENTAL ANALYSES

- ARB XRF Data
- EPA/NSI XRVF Data
- NEA XRF Data
- DRI XRF Data
- UM INAA Data

APPENDIX D - DATA FROM INTERCOMPARISON OF SCAQS FILTER ELEMENTAL ANALYSIS

- Canister Sample 108
- Canister Sample 109
- Canister Sample 146

APPENDIX E - DATA FROM INTERCOMPARISON OF PAN ANALYSIS

- EPA Data
- DGA Data

APPENDIX F - DATA FROM COMPARISON OF B-ABS WITH FINE MASS

LIST OF TABLES

<u>Table</u>		Page
1-1	Summary of SCAQS Measurements	. 1-2
1-2	SCAQS Gas Analyzer Audits	. 1-6
3-1	SCAQS Field Measurements by Measurement Specific Group	. 3-3
4-1	C-E Environmental Laboratory Audits	. 4-7
4-2	Performance Audit of C-E Analysis of Ions on Impregnated Filters	. 4-13
5-1	Field System Audit Locations	. 5-2
5-2	SCAQS Sampler Flow Audit Results	. 5-4
5-3	Summary of SCAQS Sampler Flow Audits	. 5-9
5-4	Carbonyl Flow Audit Results	. 5-11
5-5	Flow Rate Audit Results for Aerosol Particle Counters, Cyclones, and Impactors	. 5-12
5 - 6	Nephelometer Audit Results	. 5-14
5-7	Gas Analyzer Performance Audit Results	. 5-16
5-8	Performance Audit Results for Meteorological Measurements	. 5-20
6-1	Analysis of Standard Reference Materials for XRF .	. 6-5
6-2	Analysis of Iron and Aluminum by XRF and INAA	. 6-9
6-3	SCAQS Hydrocarbon Comparison Study	. 6-14
7-1	Uncertainty for SCAQS Measurements	. 7-4

LIST OF FIGURES

Figure		Page
6-1	Scatter Diagram of XRF Measurements of Silicon, Aluminum, Iron, Sulfur, Calcium, Potassium, Manganese, and Zinc Concentrations by NEA and EPA/NSI	6-6
6-2	PIXE Measurement of Concentration Gradient Across the Filter by UCD	6-8
6-3	Scatter Diagram of Hydrocarbon Concentrations (> 5 ppbC) Measured by Each Laboratory vs. The Mean	6-11
6-4	Coefficient of Variation in Hydrocarbon Concentrations vs. Mean Concentration	6 - 12
6-5	Scatter Diagram of Light Absorption Measured by Radiance Research vs. Elemental Carbon Concentrations Measured by ENSR	6 - 15
6-6	Ambient Measurement of PAN by DGA and by EPA During SCAQS	6 - 17
6-7	Relative Difference of PAN Measurements by DGA and by EPA vs. Mean Concentration	6-18

1. SUMMARY

This report reviews the results of the quality assurance (QA) program implemented for the multi-year Southern California Air Quality Study (SCAQS). The overall goal of SCAQS is to develop and archive a comprehensive air quality and meteorological data base for the South Coast Air Basin (SoCAB). The data base will be used to understand the formation of high pollutant concentrations and to evaluate, test, and improve air quality models used to simulate air quality within the study region. The QA program for SCAQS was managed by ENSR Consulting and Engineering (ENSR) and implemented with the assistance of the California Air Resources Board (ARB), the South Coast Air Quality Management District (SCAQMD), and Sonoma Technology, Inc. (STI). Table 1-1 provides a summary of the measurements which comprised the core of the measurement program and were the primary focus of the QA study.

1.1 SCAQS Quality Assurance Program

Quality assurance includes two types of activities: assurance (QA) and quality control (QC) audits. The QC activities consist of documented standard operating procedures for sample collection and analysis, data processing, and auditing. procedures define schedules periodic calibrations for They specify predefined tolerances which are performance tests. not to be exceeded by performance tests and the actions to be taken The QC activities are ongoing activities when they are exceeded. performed by measurement and data processing personnel. procedures employed during SCAQS were developed, documented and reviewed implemented by each measurement group, and for completeness by the QA auditor.

QA auditing is an external function performed by personnel who are not involved in normal operations. The purposes of the QA audits are to determine whether the QC procedures are adequate and are

TABLE 1-1
SUMMARY OF SCAQS MEASUREMENTS

						•		i sites/
	No. of	sites	A Site		i skot	I		release
8 & 8+ Site Measurements	Sum	Fell	Add'I Measurements	Sum	Fell	Other Measurements	Sum	Fall
					l		1 1	
METEOROLOGY			GASES (continuous)			METEOROLOGY	1 - 1	
Wind speed	9	6	HINO2, HCHO, NO2 (DCAS)	2	1	Revinsondes	6	5
Wind direction	9	_	H2O2, HCHO, HNO3 (TDLAS)	1	1	Airsondes	2	1
Temperature or dew point	9	6	PAN, NO2 (GC/luminol)	1	1	Wind speed/direction	1 4 1	3
UV radiation	4	2	NO3 Radical (DOAS)	1 1	0	Temperature	1 4 1	3
	1	ł	į	i l		Acoustic Sounders	2	1
GASES (continuous)	1	1	CASES		ļ		1 1	
3	9	6	(Integrated samples)	1 _ :	١.	AIRCRAFT FLIGHTS	1 .	
HO/NOx	9	6	CZ-C12 HC	3	0	LIDAR	25	3
SO2	6	6	Organic Acids	2	1 1	STI	43	0
CO	9	6	Carbonyis (add1 meas, methods)	3	1	w	9	١
PAN	9	5	Methyl & ethyl alcohol	2	1		1 1	
	1		NH3, HNO2, HNO3	1	1	PHOTOGRAPHY	3	2
GASES		Į.	Halocaroons	1	0	Time tages	3	2
(integrated samples)		۱.		1		Still photgraphs	ا د ا	-
SO2 in the	9	6	AEROSOL PHYSICAL		l	TRACER RELEASES	1 1	1
NH3 > SCAQS	9	6	PROPERTIES					
HNO3 / Sampler	9	6	Light absorption (add1 methods)	1	1 1	SF6	2	2
Carbonyis	9	6	Path transmittance & radiance	1	0	Periluorocarbons	6	''
C1-C10 HC	9	6	Long path light extinction	1	1		j i	
H2O2	4	0	Size vs. RH	1	0	1)	
Taxics	4	2	Light scattering vs. RH	2	0		1 1	
	1	1	Detailed fine part, size distribution	2	2		1 1	
AEROSOL PHYSICAL	i	i	1	1	İ		1 1	1
PROPERTIES	1 .		AEROSOL CHEMSTRY				1 1	
Size dist. (0.1-3µm)	3	2	(time resolved)			1	1	1
Light scattering	9	6	Semi-cont. aerosol carbon	1 1	1	1	1 1	1
Light absorption	9	6	Continuous suifate	2	0	1	1 (
(in SCAQS sampler)	ì	1	Black carbon	1 1	1		1 1	
	i	1	PM-10 Mass	1	1	į	} !	
AEROSOL CHEMISTRY							1 1	
PM-10/PM-2.5:	1		AEROSOL CHEMISTRY		}	Ì	1 1	
(in SCAQS Sampler)	١.	_	(integrated semples)	_	_		1 1	
Mass	9	6	Carbon 14 (PM-3.5)	3	2		1 1	- 1
SO4=	9	6	PAHs, Mutagenicity	2	1			1
NO3-	9	6	Aerosol Acidity	1	1		1 1	- 1
CI₀	9	6	Elements (PIXE, FAST)	3	2] [
NH4+	9	6	Br. Pb	1	1	•	1 1	- 1
Elements	9	6	EC, OC; SO4-, NO3-	2	1			
Elemental C	9	6	Large perticle mass, SO4=, NO3-	1	0			- 1
Organic C	9	6						l
Size Selective HiVol	9	6	SIZE RESOLVED				1 1	
Mass, SO4-, NO3-	9	6	AEROSOL CHEMISTRY (add'1)				1 1	- 1
	1	İ	Mass	1	. 0]	j
SIZE RESOLVED		l	Functional Groups	1	0		1	1
AEROSOL CHEMISTRY			S, SO4-, NO3-	1	0		, 1	- 1
SQ4-	3	2	Pb	1	0		1 1	i
NO3-	3	2					1 1	1
CI-	3	2	ACIDITY SAMPLERS				1 1	ı
H+	3	2	(SO2,HNO3,HNO2,NO2,SO4.,NO3-					
NH4+	3	2	Call. Dry Deposition Sampler	1	0		1 1	
Nae	3		Operat. Evaluation Network Sampler	1	0			
Elemental carbon	3	2	EPA Annular Denuder	1	0		1	
Organic Carbon	3	2	EPA Transition Flow Reactor	3	2]
Elements	3	2	Dry deposition Plates	. 1	0		1 1	1

being followed and whether the tolerances for accuracy and precision are being achieved in practice. The QA auditing function consists of two components: system audits and performance audits. System audits include a review of the operational and QC procedures to assess whether they are adequate to assure valid data which meet the desired levels of accuracy and precision. Performance audits establish whether the predetermined specifications for accuracy are being achieved in practice by challenging the measurement system with a known standard sample which is traceable to a primary standard.

1.2 Preliminary Audits

Preliminary audits ENSR conducted before the field study included a review of standard operating procedures and system audits administered via interviews and questionnaires. These system audits reviewed documentation procedures, data management, laboratory procedures, and QC of analyses and measurements. Facilities reviewed included:

- EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) for hydrocarbon speciation by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS)
- C-E Environmental (C-E) for ion analysis and mass measurements
- EPA and NSI Technology Services Corporation (NSI) for elemental analysis
- SCAQMD for criteria pollutants
- Tracer Technologies for perfluorocarbon tracers
- AV for the SCAQS Sampler
- EMSI for filter ion chemistry.

In addition to the preliminary system audits, a preliminary performance audit using spiked filter samples was conducted for filter ion chemistry at C-E.

1.3 Field Audits

Early during the summer study ENSR managed system audits at Azusa, Burbank, Claremont, Hawthorne, Long Beach, and San Nicolas Island, with support from the ARB QA Section and the SCAQMD Technical Services Division to perform the field measurements. The audit focused on the operation of the SCAQS aerosol/gas samplers, hydrocarbon canister samplers, carbonyl samplers, PAN samplers, and nephelometers. The purposes of these audits were to evaluate the training of operator personnel, to verify that standard operating procedures (SOPs) and QC procedures were being followed properly, to assess the completeness of onsite documentation, investigate the condition and setup of instrumentation. Audits were also conducted at Ontario Airport for upper air soundings, and aboard UW and STI aircraft for air quality and meteorological measurements.

The SCAQMD Technical Services Division and ARB QA section conducted flow rate performance audits of onsite measurement instrumentation at Long Beach, Claremont, Los Angeles (North Main), and aboard UW and STI aircraft.

1.4 Special Studies and Intercomparisons

Prior to the field study, AV operated all 10 SCAQS samplers sideby-side to verify equivalency and to determine precision of results. Because of the difficulty of defining performance audit procedures for certain measurements, ARB coordinated comparison studies for elemental analysis, speciated hydrocarbons, light absorption and peroxyacetyl nitrate (PAN).

1.5 Results of the Quality Assurance Program

The following paragraphs summarize the more significant results of the SCAQS QA program. More comprehensive details are provided in the main body of this report.

Preliminary Audits

- Operational and QC procedures for NSI's x-ray fluorescence (XRF) analysis and SCAQMD's measurement of criteria pollutants and meteorological parameters were organized, documented, and long established. No significant recommendations were made.
- Suggestions were presented to EPA for expanding technical documentation, revising data forms, formulating plans for selection of GC/MS samples, and devising replicate analyses to determine precision and the effect of sample storage.
- Operations and laboratory practices at C-E were well organized, but the ammonia/ammonium determinations on oxalicacid impregnated filters could be improved. Recommendations were made for a new filter for ammonium particle collection and modifications of the operator checklist.
- Tracer Technologies' perfluorocarbon tracer study was found to be well designed, with properly documented QA procedures and data.

Field Audits

- The audit of AV showed that operating procedures were well documented and adequately designed to minimize potential operator error. Flow audit procedures were developed. Problems discovered with nephelometer measurements, station logs at some sites, and the hydrocarbon (HC) canister sampler at three sites were rectified quickly.
- Results of the flow rate audits were good.
- Results for the performance audits of nephelometers were good except at Rubidoux, where instrument response was noisy.
- The gas analyzer audits revealed a number of problems (see Table 1-2) which were traced to calibration system errors.
 These problems were subsequently corrected.
- Sample manifolds needed cleaning at some SCAQMD sites.
- T&B upper air instrumentation was not yet operational during the audit.

TABLE 1-2

SCAQS GAS ANALYZER AUDITS

				Ave	rage Dev	Average Deviation From True (%)	m True (8)
Operator	Site	Date	Auditor	03	00	NO2	<u>CO</u> 2	THC
SCAQMD	Los Angeles	06/16/87	н	- 3.7	4.5	- 6.2	0.2	-4.7
		11/19/87	н	0.6 0.0	4.9	1.4	3.4	0.9
ARB	Long Beach	06/11/87	ч	- 4.6	- 5.9	- 6.5	28.8	
		11/17/87	٦	- 1.0	- 2.2	10.4	28.0	
GMRL	Claremont	06/18/87	н	- 4.5		- 34.0	- 20.8	
		06/27/87	Н		-56.1	- 25.2	- 22.2	
		07/03/87	7			- 40.6		
		09/04/87	င		6.6 -	- 4.5		
	Long Beach	11/17/87	н		- 1.7	1.0		
STI	Aircraft	06/22/87	1	- 3.5		- 12.1	2.8	
		11/18/87	Н	12.7		10.0		
UW	Aircraft	06/22/87	н	39.9	- 2.8	96.1	46.5	
		06/26/87	Н	88.5		84.4	50.9	
		07/27/87	4	119.2		109.1	172.1	

Auditor Key

1 = ARB Quality Assurance Section
2 - ARB Air Surveillance Branch
3 = SCAQMD
4 = Sonoma Technology, Inc.

Comparison Studies

- A discrepancy in values for soil-related elements was attributed to SCAQS sampler filter sample nonuniformity and the different areas of filter exposure by NEA and EPA/NSI.
- Results of the laboratory comparison for speciated hydrocarbon analysis were within acceptable ranges.
- Following an initial problem due to filter variability and lack of an optical tare, final audit results for optical extinction by absorption were reasonable.

1.6 Recommendations

The SCAQS QA led to general suggestions regarding the application of QA in complex research projects as well as specific recommendations regarding SCAQS measurement areas.

- Because accurate analysis of filter samples often depends on uniform filter deposits, it is important to include checks that characterize the uniformity of the sample deposit. Filter deposit profiles should be included as a standard part of filter sampler specifications.
- A forum should be established with the objective of obtaining a consensus on uniform guidelines for the reporting of speciated hydrocarbon data.
- Finally, short-term, complex field studies should include a shakedown period sufficient to conduct field system and performance audits before the studies are well underway.

The early stages of data validation for SCAQS are now in progress. Formal validation tests are being compiled for each measurement and will be applied during the second and third quarters of 1989. The mechanism is now in place within the Archive to document the identification and resolution of future data problems as well as any resulting modifications. Thus, QA will continue to be an integral part of the SCAQS program for years to come.

2. RECOMMENDATIONS

Experience obtained during the SCAQS QA Program has led to some general observations on the successful application of QA in complex research projects, as well as some suggestions relevant to specific measurement areas.

Filter Deposit Uniformity

Methods for analysis of filter sample deposits that determine concentrations from only a fraction of the filter, or that do not weight all fractions of the filter equally, obviously depend on uniform filter deposits. Measurements for which this may be true include XRF, carbon, and particle light absorption coefficient (b_{abs}). Practical samplers cannot always meet the ideal of uniform filter deposits. Thus, when characterizing a new sampler, it is important to include checks that characterize the uniformity of the sample deposit. We recommend that filter deposit profiles should be included as a standard part of filter sampler specifications.

Speciated Hydrocarbon Data Reporting

The great variety of hydrocarbon species present in polluted air, the number of assumptions required, and the individual nature of various researchers' analytical and reporting approaches, causes moderate difficulty when attempting to compare or evaluate results. Yet precisely because of this variety, QA evaluations and intercomparisons are important. We recommend that a forum be established with the objective of obtaining a consensus on uniform guidelines for the reporting of speciated hydrocarbon data. Items for consideration include:

 unambiguous and uniform naming of compounds, perhaps by including Chemical Abstract Service (CAS) registry number;

- criteria to be satisfied before a chromatographic peak is considered identified rather than unknown;
- reconciliation of total hydrocarbon measurements with the sums of identified and unidentified peaks;
- identification of standard compound classes to be reported as class totals, with completeness criteria determined from the reconciliation of speciated to total hydrocarbons;
- standardization of the treatment of different response factors to different compounds;
- standardization of conventions for reporting ppm carbon vs micrograms of reference compound per cubic meter.

This list is intended only to illustrate the kinds of issues where inconsistencies among investigators make QA more difficult. We are not recommending that uniform analytical procedures be established. We do believe that more uniformity in reporting would be beneficial to the data user.

General Observations

A good QA plan is designed to improve and "assure" data quality, not just to check data quality. As such, it is important that adequate time and effort be allocated to QA before the core sampling program is expected to produce quality data. This is especially important for complex, short-term, one-of-a-kind research studies such as SCAQS. Our experience during the SCAQS confirms our experience with QA for other large studies--QA audits almost inevitably uncover some problems. The problems can generally be resolved, and they need not have a serious impact on data quality if corrected before the study begins in earnest.

Prior to the first SCAQS sample day, considerable effort was spent on shakedown runs, sampler testing, and preliminary QA audits. This effort contributed significantly to the success of the study. However, due to time and funding constraints, many audits and intercomparisons could not be completed until the study was well underway. As a result, problems with continuous gas analyzers and

with non-uniformity of SCAQS Sampler filters were not discovered until after the study began. This led to much effort attempting to resolve problems and to correct flawed data.

The situation where problems are detected during a study can probably never be completely avoided. However, we would like to emphasize the benefits obtained through early QA, by making the following recommendation. Short-term field studies should include a shakedown period sufficient to conduct field system and performance audits before the study begins in earnest.

3. INTRODUCTION

In the summer and fall of 1987, a field measurement program was carried out in the SoCAB as part of the SCAQS. SCAQS is a multi-year, integrated air quality study whose overall goal is to develop and properly archive a comprehensive air quality and meteorological data base for the SoCAB. The data will be used to better understand the formation of high pollutant concentrations and to test, evaluate and improve elements of air quality simulation models for oxidants, NO₂, PM₁₀, fine particles, visibility, toxic air contaminants and acidic species. SCAQS is jointly funded by governmental agencies, industry groups and individual corporate sponsors. A wide range of modeling and interpretive data analysis projects are planned by various sponsors. A data archive, consisting of approximately 200,000 individual measurements from 50 groups, is expected in spring 1989.

The production of a data base for the purpose of model evaluation and testing, with the goal of control strategy and regulatory development, requires the collection of data with quantified accuracy and precision. Crucial to the determination of these attributes of a measurement is a well-defined QA program. QA encompasses those activities which complement the measurement process by providing estimates of accuracy, precision, and validity, and by ensuring that these attributes are within acceptable limits.

SCAQS Field Study

The measurement program comprised six intensive study days between June 15 and July 24, five intensive study days between August 20 and September 3, and six intensive study days between November 9 and December 11. During each measurement period, the field study included a network of existing air quality monitoring stations (C-sites); enhanced monitoring stations (nine during the summer

period and six during the fall period) located along typical air trajectories to routinely measure aerosol and gases on intensive days (B-sites); one research station each in a source and receptor region in the summer and one station in a source region in the fall (A-sites); a network of stations for meteorological measurements at the surface and aloft on intensive study days; upper air pollutant and light detection and ranging (LIDAR) measurements by aircraft on intensive study days; measurement of selected toxic air contaminants at selected sites; physical and chemical measurements of fog and clouds on intensive study days; special studies on selected study days, including multiple tracer releases; assembly and archiving of supplemental data from existing sources; and a QA program including independent systems and performance audits.

The number of organizations participating in the SCAQS, and the diversity of measurements conducted are tremendous. To prevent this situation from becoming overwhelming, the SCAQS measurements have been classified into a number of measurement areas, and a Measurement Specific Manager (MSM) has been assigned to each area. The MSMs are responsible for overseeing the consistency and quality of data within their areas. The SCAQS measurements, broken down by measurement area, are listed in Table 3-1. The measurements made at the B-sites represent the core of the measurement program and were the primary focus of the QA program.

Quality Assurance

The QA auditing program for SCAQS consists of two components: system audits and performance audits. System audits include a review of the operational and QC procedures to assess whether they are adequate to assure valid data which meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine whether the procedures are being followed and the operating personnel are properly trained. The system audit is

TABLE 3-1

SCAQS FIELD MEASUREMENTS BY MEASUREMENT SPECIFIC GROUP

Measurements

PI

Laboratory

10	Acoustic Sounder (book of pictures) Routine Ground Based Met Data Routine Ground Based Met Data AV 2000 Doppler Acoustic Sounder Mechanical Met - Catalina Island Rawinsondes Airsondes Airsondes Mechanical Met Stations Sea Temp., Air Temp., Upper Air Temp. Turbulence Upper Air WS WD Turbulence, Surface Met San Nicolas Island Summer 87 Soundings for FIRE NWS Upper Air: Edwards, Vandenburg	CRITTERIA, WS/SD, T/DP, TSP, BSCAT O3, CO, NO, NO, SO2, WS/SD, T/DP, RAC Tape Sampler Eppley UV Photometer Dasibi Model 2008 Photometric NO2 Analyzer O3, CO, NO, NO, WS/SD, T/DP, TSP MRI #1561 Nephelometer (Heated Inlet) MRI #1561 Nephelometer (Heated Inlet) Eppley UV Radiometer Andersen SSI (PM ₁₀), Hivol, SO ₄ , NO ₃ CO, BSCAT, O ₃ , NO, NO ₂ , NO ₈ , SOLARAD, UVRAD DWPT, RH, TEMP, TEMP5, TEMP5, TDIFF, V_WD, V_WS, WS
Measurements tt, (916) 323-1506	Wolff Croes Croes Ellis/Filek Blumenthal Lehrman Lehrman Croes Croes Croes	ria Gases, Bs (916) 323-15 Bope Kowalski Kowalski Jung Chan Chan Croes/Bope Chan Eden Wolff
Meteorological Measurements Chuck Bennett, (916) 323	GM NWS SCAQMD SCE/AV STI-B TBS TBS TBS TBS/STI Navy Penn St. FIRE	B-Site: Crite Bart Croes, AQMD ARB-HS ARB-HS AV AV AV AV AQMD AV AQMD AV AQMD GM GM

Measurements	and Toxics	ARB Tedlar Bags for Toxics Biospherics Canisters C ₁ -C ₁₂ Biospherics Canisters C ₁ -C ₁₂ Biospherics Canisters DNPH Cartridges: Carbonyls Formic Acid, Acetic Acid, by Alkaline Cartridges L Ar Trap, Aldehydes, Ketones HC Canisters Aldehydes (DNPH SEP Packs) GC and GC/MS for Canisters GGC Carbon Cartridges for Alcohols DOAS for HCHO (also listed with HNO ₃ -NO ₂) UN/STI Aircraft: Hydrocarbons UW/STI Aircraft: Carbonyls	PAN by GC, Electron Capture PAN - Integrated Measurement for UW and STI Aircraft PAN (GC-ECD) UD GC - luminal detector for PAN UW/STI Aircraft: Pan	$\rm H_2O_2$ Impingers Hydrogen Peroxide Unisearch TDLAS for $\rm H_2O_2$ (listed above with HNO_3 meas.)
PI	, Aldehydes,) 323-1533	Croes Rasmussen Rasmussen Knapp Taketomo Grosjean Lev-On Lonneman/Ellenson Knapp Kaplan Winer MacKay	(916) 323-1533 Grosjean Grosjean Lonneman/Ellenson Stedman	e (916) 323-1533 Lev-On Ellis/Kaplan MacKay
Laboratory	Gases: Hydrocarbons Eric Fujita, (916	ARB-HS Bio Bio EPA ENSR DGA EMSI EPA-GKP EPA-GKP EPA-GKP COC UCR UCR UNISCH EPA/STI/UW ENSK/STI/UW	Gases: PAN Eric Fujita, DGA DGA EPA-GKP UD DGA/STI/UW	Gases: Peroxide Eric Fujita, EMSI SCE-UCLA Unisch

Measurements

Laboratory

	n Monitor Labs 8840 NO, with Nylon Prefilter DOAS for NO, HNO, HCHO, NO, UD Luminol Detection of HNO, Unisearch TDLAS for Formaldehyde, H ₂ O ₂ , HNO, Particle Sulfate Total Strong Acid, pH HONO, M73, HNO, NH, O ₃ , NO/NO, with Na ₂ CO ₃ Denuder	Aircraft Filters 9372	SCAQS Sampler Field Sampling Data SCAQS Sampler Ion Chemistry Filter Loadings SCAQS Sampler Carbon Filter Loadings SCAQS Sampler B-abs Filter Loadings SCAQS Sampler XRF Ambient Concentrations SCAQS Sampler, SSI Hivol Aircraft: Aerosol Filter Chemistry Aircraft: Aerosol Filter Chemistry	ling 2 Low-vol and Hivol Quartz Filters for Organics	Cumulative OC, EC Size Distributions, Nighttime Pb/Br IMPROVE Cyclone Filter Samples/PIXE Dichots for Carbon, Mass, XRF, NO3, SO, SSI Hivols, Hivols, Tenax Columns, and PUF for PAHs
$ ext{HNO}_3$, $ ext{NO}_2$, and $ ext{Other}$ $ ext{Fjuita}$, $ ext{(916)}$ 323-1533	Lonneman/Ellenson Winer Stedman MacKay Appel Appel Appel	SCAQS Sampler and Airc Hering, (707) 527-9372	Chan Countess Taketomo Weiss Knapp Wolff Anderson	Filte Herin	Turpin Turpin Nakamura Main Atkinson
Gases: HNC Eric Fju	EPA-GKP UCR UD UDISCH AIHL AIHL AIHL	Aerosols: Susanne	AV EMSI ENSR RR EPA GM STI Others/UW	Aerosols: Susanne EPA-SSB	GGC OGC UCD UCLA-2 UCR

Laboratory	y PI	Measurements
Aerosols: S Susanne H	Size Resolved Chemistry Hering, (707) 527-9372	
AIHL UCLA-1 UCLA-1 UCLA-2 UM UM	John Allen Nakamura Allen Main McMurry McMurry	Berner Impactor for Inorganic Ion Size Distributions Low Pressure Impactor/FTIR UCD Drum Impactor for PIXE (Elemental Distributions) LPIS for FTIR Functional Groups, S and NO ₃ LPI for Pb Distributions MOUDI for OC, EC MOUDI for Mass Rh-controlled Tandem DMAs, Reaction and Growth DMAs
Aerosols: I Susanne H ARB-Sacr. OGC	n Situ Chemistry ering, (707) 527- Croes Huntzicker Huntzicker	Measurements 9372 MDA BAM Sampler (Beta Gauge) Continuous Sulfate In Situ Carbon
Aerosols: P Susanne H AV UM	Physical Size Distributions Hering, (707) 527-9372 Moon McMurry/Hering Reischl	ons Climet 208 OPC, PMS LASX Probe, TSI 3030 EAA DMA/OPC Calibrations Classifier for Fine dN/dDp
Visibility P Susanne H	Parameters Hering, (707) 527-9372	
Ford Ford LBL STI-R UI UV	Adams Adams Hansen Richards Rood Hitzenberger	Spectrophone Nephelometer, Filter for Black Carbon Aetholometer Path Transmittance and Radiance UI RH-Temp. Controlled Nephelometer Measurements Nuclepore Filter for Babs Telephotometer-10 Wavelengths, Babs by Nuclepore Filter

Measurements		Denuder Difference for HNO ₃ , NO ₃ - Annular Denuder (on roof) Transition Flow Reactors for Inorganics OEN Acid Sampler		Dry Deposition Foils Dry Deposition Onto Plants Rotary Impactor for Coarse Particles Deposition Plates	Nephelometer, Met, Position	Dasibi 1003: O ₃ Aloft - Aircraft Aircraft: O ₃ , CO, NO, NO _x , SO ₂ , T/DP, Position, Altitude Aircraft: MRI #1569 Neph., PMS ASASP-X Aer Size Dist Aircraft: O ₃ , NO, NO _x , SO ₂ , T/DP, BSCAT, Position, Alt.		GM Smog Chambers City of Hope Aerosol Samp. and Organic Reactivity Studies Dichotomous Samplers, PM _{3.5} Hivol Denuder Quartz Filters Edison Van: O ₃ , CO, NO, NO _x , SO ₂ , WS/SD, T/DP Edison Van Beckman Dichot.
Id	dic Particle and Vapor Samplers Lowell Ashbaugh, (916) 323-1507	Horrocks Ellenson Knapp Heisler	tion Measurements Ashbaugh, (916) 323-1507	Davidson Davidson Noll Noll	- Gases,) 323-1534	Bennett Anderson Anderson Hegg	es (916) 323-1534	Nelson Kaplan Kaplan Kaplan Gains
Laboratory	Acidic Particle and Lowell Ashbaugh,	ARB-HS EPA-GKP EPA-SSB ENSR	Dry Deposition Measurements Lowell Ashbaugh, (916) 3	CMU DMU IIT IIT	STI and UW Aircraft Bart Croes, (916	ARB-Sacr. STI STI UW	Special Studies Bart Croes,	GM SCE-GGC SCE-GGC SCE-GGC SCE/AV SCE/AV

Measurements		Cloud/Fog Water Chemistry Fog Samples		Aircraft Lidar Measurements SF6 Tracer Releases and Sampling Urban Tracers Perfluorocarbon Tracers		Time Lapse 16mm Motion Pictures (3 sites) Still 35mm Photos (2 views at each of 3 sites)		Day-specific Emissions Inventories Tunnel Sampling - Emissions Inventory Tunnel Sampling - Automotive Pb Distributions
Ιœ	Phase Studies , (915) 323-1533	Hoffman Kaplan	Tracers and Lidar Aircraft Chuck Bennett, (916) 323-1506	McElroy Shair D. Miller Ellis/England	, (916) 324-8496	Richmond Richmond	Source Profiles (916) 322-6021	Oliver Ingalls Friedlander
Laboratory	Fog and Liquid Phase Eric Fujita, (915)	CIT-Fog SCE-GGC	Tracers and Lidar Chuck Bennett,	EPA-LV CIT DRI SCE-TT	Photography Doug Lawson,	RP RP	Emissions and Source Gary Agid, (916)	Radian SW UCLA-2

a cooperative assessment resulting in improved data. System audits were conducted for:

- hydrocarbon speciation,
- SCAQS filter sampler,
- SCAQS filter ion chemistry,
- SCAQS filter XRF analysis,
- criteria gas measurement,
- tracer studies, and
- field system audits.

Performance audits establish whether the predetermined specifications for accuracy are being achieved in practice. For measurements, the performance audit involves challenging the measurement/analysis system with a known standard sample that is traceable to a primary standard. Performance audits of data processing involve independently processing samples of raw data and comparing the results with reports generated by routine data processing. Performance audits were conducted for:

- Flow rates for the SCAQS Samplers, carbonyl samplers, aerosol particle counters, impactors, and size-selective inlet (SSI) Hivols;
- continuous analyzers for O₃, SO₂, NO₂, CO, THC, and CH₄;
- nephelometers; and
- meteorological measurements.

The specialized nature of many measurements conducted during the SCAQS precluded simple performance audits for these measurements. Core measurements that fall into this category include XRF, hydrocarbon speciation, b_{abs} , PAN, and upper air meteorological soundings. Intercomparison studies were used to assess the representativeness, accuracy, and precision of these measurements. In addition to these studies, a special study was conducted to

assess the performance of the newly designed SCAQS Sampler before the study began.

Report Organization

The QA activities performed for the SCAQS have been broadly grouped into the following categories:

- preliminary audits,
- field audits, and
- special studies and intercomparisons, and
- discussion of measurement accuracy and precision.

Each of the subsequent chapters of this report, covers a specific category of activity. Within these chapters, the descriptions of QA methods, results, follow-up, and conclusions, are grouped together for specific QA activities. The results and conclusions, and the recommendations resulting from each activity, are presented in the Summary and Conclusions, and the Recommendations chapters.

4. PRELIMINARY AUDITS

After review of SOPs, preliminary system audits were conducted for:

- hydrocarbon speciation by GC/GC-MS (EPA AREAL),
- elemental analysis by XRF (EPA/NSI),
- criteria pollutants (SCAQMD),
- perfluorocarbon tracers (Tracer Technologies),
- the SCAQS Sampler (AV) and
- filter ion chemistry (EMSI).

The system audits were conducted through review of SOPs, interviews, and completion of detailed questionnaires. These audits were conducted at the measurement laboratories for EPA, EPA/NSI, AV, and EMSI, and through telephone interviews for the SCAOMD and for Tracer Technologies.

The system audits addressed issues including documentation, training, analytical methodologies, instrumentation, sources and preparation of reagents, standards, work space, sample handling, data processing, QC, and use of QC data. The objective of the system audits was to review planned measurement methods to ensure that they produced data that met the quality objectives of the SCAQS program. The review had four main components:

- technical adequacy of the method to meet desired objectives for sample integrity, and for data precision, accuracy, and detection limits;
- a QC plan to demonstrate sample integrity and data precision;
- adequate documentation for technical assessment by eventual users of the data;
- adequate documentation for personnel conducting the measurements.

objective of system audits Another the was to provide performance audit or test to recommendations for a assess The "results" of the preliminary system measurement accuracy. audits consisted of suggestions and recommendations to enhance the measurement plan.

In addition to the preliminary system audits, a preliminary performance audit was conducted for filter ion chemistry analyses at EMSI. The performance audit consisted of challenging the EMSI laboratory with spiked filter samples.

4.1 Hydrocarbon Speciation

On May 8, 1987, John Collins and Kochy Fung of ENSR visited Ken Knapp and Len Stockburger at the EPA AREAL in Research Triangle Park, North Carolina. At this time procedures for hydrocarbon speciation were still in development. Our recommendations were to:

- document procedures to a level of detail adequate for subsequent technical review,
- prepare sample handling and data forms,
- develop an explicit plan for the selection of GC-MS samples,
- design explicit procedures that would be used to determine the precision of field data.

Technical documentation, data forms, a plan for selection of GC-MS samples, and a plan for replicate analyses to determine precision and sample storage effects were eventually formalized.

The audit revealed that the accuracy of hydrocarbon data from any GC system designed to quantify a large number of species is affected by choice of standards, assumptions about response factors, and by difficulties in peak identification. Because these issues cannot be addressed by a simple performance audit, an

intercomparison study was recommended. The results of the intercomparison study are given in Chapter 7.

4.2 XRF Analysis

On May 8, 1987, John Collins visited Ken Knapp and Bob Kellogg at the EPA/NSI Laboratories in Research Triangle Park, North Carolina. Procedures for XRF analyses at this laboratory were well established. Sample handling, analytical procedures, data processing, and QC appeared to be of high quality and were well organized and well documented. No significant recommendations were made as a result of this audit.

The audit revealed that measurement accuracy cannot be easily assessed by a simple performance audit due to assumptions regarding particle size distributions and other matrix effects. An intercomparison involving SCAQS samples, NIST (formerly NBS) standards, and Micro-Matter standards was recommended. The results of the intercomparison are given in Chapter 7.

4.3 Criteria Pollutants and Meteorology

On June 19, 1987 John Collins conducted a telephone interview with Bill Bope of the SCAQMD. The District operates the air quality monitoring stations in compliance with EPA QA/QC requirements for National Air Surveillance Network (NASN) stations. Each station is audited annually by an independent group within SCAQMD. In addition, selected stations are audited each year by the QA section of the ARB.

The interview demonstrated that existing procedures and routine operations are sufficient to meet the needs of the SCAQS. The only recommendations were to clean all sample manifolds before the study began, and to ensure that station operators receive special training if they will operate any new equipment special to the SCAQS.

Performance audits would be obtained by arranging a special visit of the ARB QA section auditing team.

4.4 Perfluorocarbon Tracer Study

A preliminary system audit of the perfluorocarbon tracer study was conducted through review of the Quality Assurance Plan prepared by through telephone interview Tracer Technologies, and Mr. Thomas Rappolt, Tracer Technologies QA Manager for the study on May 14, 1987. Issues addressed by the review included release system calibrations, sampler calibrations, expected detection sample handling and identification, limits. field procedures, operator training, and logistics. The review and interview demonstrated that the study was well designed, incorporated well documented QA procedures and data. specialized nature of the measurements, no field performance audit procedures were developed.

4.5 SCAQS Sampler and SCAQS Sampler Ion Chemistry

Preliminary audits for SCAQS Sampler filter chemistry involved both system and performance audits. ENSR reviewed methodology, reviewed side-by-side SCAQS Sampler testing results (described more fully in Chapter 6, Special Studies and Intercomparisons), visited the chemistry laboratory, visited field operations headquarters, helped design performance audits for laboratory and field operations, and helped interpret performance audit results. The QA efforts combined effectively with the final stages of method development and testing, to significantly improve the sampling and analysis method.

On May 29, 1987, Chris Lanane of ENSR visited Alex Barnett of AV to review SCAQS Sampler operation and documentation, and to develop a flow rate performance audit procedure. The audit showed that operating procedures were well documented, and that the procedures,

as well as the sampler itself, were adequately designed to minimize potential for operator error. The operators were receiving training on the sampler in the course of final sampler testing. Flow audit procedures were developed.

On June 11, 1987, John Collins and Barbara Wright of ENSR visited Richard Countess of C-E at C-E's facilities in Camarillo, California. The auditors reviewed procedures for filter sample and denuder preparation, filter kit preparation, filter numbering, determinations. extraction procedures, mass sample logging, analytical instrumentation and reagents, calibration procedures, and data recording and data reduction. Overall, the operation appeared well organized and good laboratory practice was followed Accuracy, precision, and detection limits for the SCAQS Sampler collection and analysis were as yet undemonstrated. Results of the side-by-side precision testing and the performance audits would be used to demonstrate the adequacy of the SCAQS Sampler collection and analysis to meet the needs of the SCAQS.

A review of methodology and results of precision testing indicated that accuracy, precision, and detectability of ammonia/ammonium determinations on oxalic acid impregnated filters could be significantly improved. As a result, a new filter was selected for ammonium particle collection, and prevention of contamination to active filters was given extra attention. Review of precision testing results uncovered a number of anomalous data values that were ultimately attributed to specific operator errors that occurred because the operators were still being trained while conducting the precision tests. The problems could have been detected and corrected in the field with additional checks. ENSR recommended specific operator checks of filter deposit and filter holder tightness when unloading the filter holders in the field, and these were incorporated into the operators' checklist.

Laboratory performance audits were conducted by evaluating C-E's analysis of filters spiked with known amounts of ions. The audit

took several iterations as problems were discovered and corrected, and eventually demonstrated good analytical results by C-E. A summary of the results is given in Table 4-1. More detailed results are shown in Appendix A. The following is a chronological description of the C-E performance audit.

C-E prepared filters for field use, including impregnated filters, and transmitted them to Columbia Scientific Inc. (CSI). CSI spiked replicate sets of filters and returned a number of sets to C-E for analysis. When C-E analyzed these filters, it was discovered that: results for nitrate on nylon filters were good, but problems occurred with CSI's spiking procedures for Teflon filters, with C-E's analysis for SO₄ on potassium carbonate impregnated filters, and with C-E's analysis for NH₄ on oxalic acid impregnated filters. A subsequent analysis of the CSI spiked filters by ENSR's laboratory confirmed problems with CSI's Teflon spikes and with C-E's analysis of impregnated filters.

Rather than preparing a new set of Teflon spikes, a set of Teflon filter samples from the precision testing being conducted by AV was split between C-E and ENSR for analysis of SO₄, NO₃, and NH₄. The results, summarized in Table 4-1, are given in Appendix A. The results indicate very good agreement between laboratories for ions on Teflon filters.

After review of analytical procedures for ions on impregnated filters, improvements in calibration procedures were suggested, and a new round of audit spiking was initiated. C-E prepared a number of impregnated filters and forwarded them to ENSR for spiking. ENSR spiked these filters and verified quantitative recovery using the extraction and analysis methods employed by C-E. C-E analyzed a number of these spikes and demonstrated reasonable results for NH₄ on oxalic acid impregnated filters, but results for SO₄ on carbonate impregnated filters were still inadequate.

1200-004-001

TABLE 4-1

C-E ENVIRONMENTAL LABORATORY AUDIT

Nitrate Off Nylon Filters

Ĭ	Prec. µg/fil	Meas. ug/fil	Corr. ug/fil	Dev. (%)	Aver.	(%)
00.		1.15	77.		CT.	
3.96	.01	5.18	4.30	8.6	4.39	10.7
3.96	.01	5.35	4.47	12.9		
5.90	.10	18.13	17.25	8.5	17.10	7.5
5.90	.10	17.83	16.95	9.9		
9.30	.30	80.60	79.72	5	79.82	.7
9.30	.30	80.80	79.92	ω.		
		. 88				

TABLE 4-1 (Continued)

Sulfate Off Carbonate Impregnated Filters

Dev.			3.7		- 5.0		1.7							- 4.4		- 7.5		- 3.7		
Aver.		.03	4.19		9.61		51.42					.72		3.86		9,35		48.70		
Dev. (%)			- 3.0	•	- 3.7	•	9							•	۰	- 7.5	•	•	6.	
Corr. µg/fil		.08	6	4.	9.74	4.	۲.	1.7				.84	.60	7	σ	9.35	$^{\circ}$	7.3	0	
Meas. µg/fil		69.	•	ນ	10.35	0	ä	2	.61			6.	, 7	ω	۲.	0.4	₽.	8.4	\vdash	Ċ.
Ref. Prec. ug/fil	ISI		.01	.01	.03	.03	.17	.17			Lab-CSI			.01	.01	.03	.03	.17	.17	
Ref. µg/fil	Ref. Lab-CSI	000.	4.04	4.	10.11	0	0	0			1987, Ref.	00.	00.	•	•	0	•	Ö	0	
Sample ID	July 1987,	405	437	442	451	462	484	492	Lab Blank		September 1	407	413	435	445	461	466	485	493	Lab Blank

Sulfate Off Carbonate Impregnated Filters (Continued)

		Ref.				Ave.				Ave.
Sample	Ref.	Prec.	Quad	Dev.	Ave.	Dev.	Linear	Dev.	Ave.	Dev.
OT.	111/57	111/67	• 100110	101	777/50	78				
November 1987, Ref. Lab-ENSR	37, Ref.	Lab-ENSR								
13	00.		53.44				51.17			
14	00.		1.81				1.34			
15	00.		-1.17							
16	2.21	.04	. 65	- 70.6			2.08	- 5.9		
17	2.21	.04	17.72	701.8				804.1		
18	2.21	.04	.62	- 71.9				-31.2		
19	6.37	.25	5.91	- 7.2	5.65	-11.3		1.1	6.03	- 5.4
20	6.37	.25	5.72	- 10.2				- 6.4		
21	6.37	.25	5.33	-16.3				- 10.8		
22	16.48	06.	16.19	- 1.8	14.87	9.8	16.40	٠.	15.80	- 4.1
23	16.48	06.	13.71	- 16.8			15.80	- 4.1		
24	16.48	06.	14.71	- 10.7			15.20	- 7.8		
Lab Blank							1.00			

Original calibration is a quadratic fit for point from .1 to 25 $\mu g/ml$. Audit samples spanned .2 to .5 $\mu g/ml$. Revised data used three calibration points between 0 and 1 $\mu g/ml$ plus zero and linear fit. Note:

TABLE 4-1 (Continued)

Ammonium Off Oxalic Impregnated Filters

Dev. (%)			- 28.6		- 44.2		- 48.8							0.6		5.6		- 7.5	
Aver.		.23	1.42		3.34		10.22					.26		2.17		6.32		18.46	
Dev. (%)			4.0	•	- 22.9	ω.	•	9						7.5	10.6	æ. 1	12.0	- 12.7	- 2.2
Corr. ug/fil		.21	2.07	.77	4.61	2.06	99.6	10.78	.16	.42		.39	.12	2.14	$^{\circ}$	5.93	7	17.41	19.51
Meas. 49/fil																			
Prec. µg/fil	ISI		.01	.01	.02	.02	.07	.07			Lab-CSI			.01	.01	.02	.02	.07	.07
Ref. Ref. µg/fil	ef. Lab-C		•	•	5.98	•	•	6			17, Ref.			0	9	9	0	19.95	ο. Ο
Sample ID	July 1987, Ref. Lab-CSI	305	306 339	340	361	362	391	392	Blan	Blan	September 1987, Ref. Lab-CSI	304	303	341	342	355	356	393	394

1200-004-001

Ammonium Off Oxalic Impregnated Filters (Continued)

9.6 3.2 33.3 Dev. Ave. (%) 1 6.75 .16 3.48 16.59 ug/fil Ave. 18.0 9. 17.2 11.0 3.4 41.0 38.3 20.7 Dev. (%) 6.20 17.72 14.04 18.00 .10 3.61 3.15 7.22 6.84 .90 . 24 3.68 Linear Cor. ı 2.0 10.9 33.8 Ave. Dev. (%) 3.49 .10 6.83 16.78 ug/fil Ave. 4.6 1.6 17.0 41.8 6.3 38.7 21.1 18.7 12.3 Dev. (%) ı 6.92 .17 3.62 3.16 17.92 6.26 .18 3.70 7.31 14.22 18.21 Uncor. Onad ı Lab-ENSR .10 .10 .08 .08 .08 .15 .15 ug/fil Ref. Prec. November 1987, Ref. 6.16 17.13 17.13 17.13 00. 00. 2.61 6.16 6.16 ug/fil 2.61 2.61 Ref. 14 15 16 17 18 19 20 21 22 23 Sample

Audit samples 0 and 1 $\mu g/ml$ a quadratic fit for point from .1 to 25 $\mu g/ml$. Audit Revised data used three calibration points between 0 and Original calibration is plus zero and linear fit spanned .2 to .5 µg/ml. Note:

Lab Blank

Further review of analytical procedures suggested improvements in data reduction procedures. C-E adopted these procedures, and subsequent application of the new data reduction procedures to earlier audit data showed good results for SO₄ on carbonate impregnated filters.

Table 4-2 shows C-E's final results for impregnated filters spiked by ENSR. Due to a communications mixup, the audit concentrations were about a factor of 10 lower than concentrations expected during SCAQS intensives. Thus, the erratic behavior at low levels in the carbonate impregnated filter audit, and the small positive offset in the oxalic impregnated filter audit, were not considered major problems. In view of program time constraints, and the significant improvements in analytical methods already achieved, auditing was concluded.

TABLE 4-2

PERFORMANCE AUDIT OF C-E ANALYSIS OF IONS ON IMPREGNATED FILTERS

Sulfate on Carbonate Impregnated

ENSR	ENSR SPIKE		G−E	
SO, μq/filter	Precision µg/filter (%)	Recovery µg/filter	Mean µg/filter % Recov.	Precision µg/filter (%)
00.0	NA	53.44 1.81 - 1.17	NA	NA
2.21	0.04	0.65 17.72 0.62	NA	NA
6.37	0.25 4%	5.91 5.79 5.33	5.68 89%	0.31 5%
16.48	0.90	16.19 13.71 14.71	14.87 90%	1.25 8%

for concentrations study. Thus, the Due to a communications mixup, audit samples were prepared approximately 10 times lower than expected during the SCAQS unresolved erratic behavior at very low levels was discounted. Note:

TABLE 4-2 (Continued)
Ammonium on Oxalic Impregnated

ENSR SPIKE	SPIKE		CI I	E)
so, ug/filter	Precision µg/filter (%)	Recovery <u>ug/filter</u>	Mean µg/filter % Recov.	Precision µg/filter (%)
0.00	NA	1.02 0.92 0.57 0.52 ^b	0.80	0.23
2.61	0°10 %	3.56 3.64 3.10	3.44 132%	0 8 8 8 8
6.16	0.08	6.20 7.25 6.86	6.77	0 .0 .0
17.32	0.15	17.86 14.16 18.15	16.73 97%	2.22

^a Blank corrected by 0.80 $\mu g/filter.$ ^b Laboratory blank.

5. FIELD AUDITS

Field performance audits were conducted for continuous gas analyzers, meteorology, nephelometers, and sampler flow rates. The performance audits were managed by ENSR and utilized the support of the ARB QA Section and the SCAQMD Technical Services Division (TSD) to perform the field measurements. In addition, ENSR personnel conducted field system audits at the monitoring locations.

5.1 Field System Audits

ENSR conducted system audits early during the summer study at the locations shown in Table 5-1. The auditor interviewed the station operator for general knowledge of air quality monitoring, knowledge knowledge of the particular SCAOS program, and instrumentation for which the operator was responsible. The audit focused on the SCAQS Sampler, the hydrocarbon canister sampler, the carbonyl sampler, the PAN sampler, and nephelometers, additional measurements were evaluated at some sites. interviewing the operator, the auditor observed the operator perform routine duties such as SCAQS Sampler filter change Onsite documentation was reviewed for completeness, procedures. and the condition and setup of SCAQS instrumentation were QC procedures and data for continuous gas analyzers evaluated. were also evaluated.

The results of the system audits are summarized below.

- Operator knowledge of all procedures and schedules was good at all locations except for nephelometer measurements. AV's training, scheduling and handling procedures were excellent.
- Onsite documentation and data recording forms were good at all sites except that station logs were not available at some sites.

TABLE 5-1
FIELD SYSTEM AUDIT LOCATIONS

Audited	Location	<u>Audit Date</u>
Core Measurements Core Measurements	Azusa Burbank	06/19/87 06/20/87
Core Measurements Core Measurements	Claremont Hawthorne	06/19/87
Core Measurements	Long Beach	06/20/87 06/17/87
Core Measurements	San Nicolas Island	06/15/87
T&B Systems STI Aircraft UW Aircraft	Ontario Airport Ontario Airport Ontario Airport	06/20/87 06/20/87 06/20/87
SCAQMD	Telephone Interview	06/19/87

- Instrument setup and location were good at all sites with the exception of the HC canister sampler at three sites. Sample manifolds needed cleaning at some SCAQMD sites.
- T&B upper air instrumentation was not yet operational at time of audit.

AV quickly rectified all the identified problems.

5.2 Flow Rate Performance Audits

The SCAQMD TSD conducted flow rate performance audits for SCAQS samplers and carbonyl samplers. In addition to these core samplers, the SCAQMD TSD also audited flow rates for the DRUM and MOUDI, and the Climet OPC, PMS Probe, and TSI EAA aerosol particle counters. The ARB QA Section audited flow rates for Hivols and SSI PM₁₀ Hivols, including SSI PM₁₀ Hivols installed and calibrated by SCAQMD TSD at the Long Beach and Claremont A-sites.

SCAOS Sampler

Results for audits of SCAQS Sampler flow rates are shown in Table 5-2 and summarized in Table 5-3. The results are generally very good. Differences between AV and the audit values are almost always within 10 percent, with the following exceptions. channel 2, showed a difference of \pm 12 percent in three out of ten The summer audit at Downtown Los Angeles showed a audits. consistent difference of about 16 percent for sampler channels 7 through 12, but these large differences were not observed during the fall audit of this site. There are not sufficient audit values quantitative calculation precision of allow The audit values are only used to assess the measurements. reliability of flow precision calculated by AV from routine QC data.

TABLE 5-2

SCAQS SAMPLER FLOW AUDIT RESULTS

TABLE 5-2 (CONTINUED)

SCAQS SAMPLER FLOW AUDIT RESULTS

						SCAGHD						
					HOMINAL	AUDIT	ROTAMETER			\		DELTA
SITE	DATE	SAMPLER	SAMPLER 1D	10 TYPE	FLOV	FLOJ	READING	SLOPE	INTERC.	FLOU	DELTA	PERCENT
RIDRANK	07/01/87	SCAOS	CHAN. 1	NATON	9-13	10.30	10.75	0.992	-0.077	10.59	0.29	2.7%
		=	CHAN. 2F		20-25	23.50	21.75	1.004	1.655	23.49	-0.01	-0.03%
		=	CHAN. 28	5	20-25	23.50	21.73	1.004	1.655	23.49	-0.01	-0.03%
		=	CHAN. 3	_	8-10	8.40	8.8	0.992	-0.077	8.80	0.40	4.78%
		=	CHAN. 4		8-10	8.90	9.55	0.992	-0.077	6.40	0.50	5.58%
		=	CHAN. 5	0		7.00	4.30	0.992	-0.077	4.19	0.19	4.72%
		=	CHAN. 6			7.90	5.20	0.992	-0.077	5.08	0.18	3.70%
		=	CHAN. 7		32-37	35.60	34.25	1.004	1.655	36.04	0.44	1.24%
		=	CHAN. 8	-	32-37	36.10	35.00	1.004	1.655	36.80	0.70	1.93%
		=	CHAN. 9F		32-37	34.80	33.50	1.004	1.655	35.29	0.49	1.41%
		=	CHAN. 98		32-37	34.80	33.50	1.004	1.655	35.29	0.49	1.41%
		=	CHAN. 10		32-37	35.60	34.50	1.004	1.655	36.29	0.69	1.95%
		=	CHAN.11	Ξ	32-37	35.60	34.65	1.004	1.655	36.44	9. 8.	2.37%
		=	CHAN. 12		32-37	35.60	34.90	1.004	1.655	36.69	1.09	3.07%
		:		DENUDER	3-5							
-	78/01/70	30473	CUAN	20.23	0-13	10, 10	11.00	0.968	0.121	10.77	0.67	6.62%
CAIN L.A.	10/11/10	3 =	CHAN		20-25	21.60	23.00	0.958	2.033	24.07	2.47	11.42%
		=	CHAN. 2	ີ ໝ	20-25	21.60	23.00	0.958	2.033	24.07	2.47	11.42%
		=	CHAN		8-10	8.80	8.85	0.968	0.121	8.69	-0.11	-1.28%
		=	CHAN. 4		8-10	8.30	8.65	0.968	0.121	8.49	0.19	2.34%
		=	CHAN.	Ö		4.00	4.10	0.968	0.121	4.09	0.09	2.24%
		=	CHAN. 6			4.70	4.70	0.968	0.121	4.67	-0.03	-0.63%
		=	CHAN. 7		32-37	31.60	35.75	0.958	2.033	36.28	4.68	14.81%
		=	CHAN. 8	F		31.00	35.25	0.958	2.033	35.80	4.80	15.49%
		=	CHAN. 9F	PF TEFLON	32-37	30.70	35.00	0.958	2.033	35.56	4.86	15.84%
		=	CHAN. 98	98 QUARTZ	32-37	30.70	35.00	0.958	2.033	35.56	4.86	15.84%
		=	CHAN. 10	O QUARTZ	32-37	30.50	35.00	0.958	2.033	35.56	5.06	16.60%
		=	CHAN.11	1 TEF.PREWGD		31.30	36.00	0.958	2.033	36.52	5.22	16.68%
		=	CHAN. 12	2 TEFLON	32-37	32.60	37.50	0.958	2.033	37.%	5.38	16.44%
		=		DENUDER	3-5							

TABLE 5-2 (CONTINUED)

SCAQS SAMPLER FLOW AUDIT RESULTS

						SCAGMD						
					NOMINAL	AUDIT	ROTAMETER			٩		DELTA
SITE	DATE	SAMPLER	SAMPLER 10	TYPE	FLO4	FLOU	READ ING	SLOPE	INTERC.	FLOS	DELTA	PERCENT
DNTH L.A.	11/09/87	SCAQS	CHAN. 1	NAFON	9-13	8.25	9.25	1.003	-0.07	9.20	8.0	11.55%
		=	CHAN. 2F	ZFLOUR	20-25	23.93	23.00	0.981	1.78 \$	24.36	0.43	1.78%
		=	CHAN. 28	CARBONATE		23.93	23.00	0.981	1. 78	24.36	0.43	1.78%
		=	CHAN. 3	NATON		7.01	7.35	1.003	-0.075	7.30	0.29	760.7
		=	CHAN. 4	NALON		7.50	7.85	1.003	-0.075	7.80	0.30	3.98%
		=	CHAN. 5	OXALIC ACD		3.85	3.90	1.003	-0.075	3.8	-0.01	-0.35%
		=	CHAN. 6	POLYCARB.		4.85	4.90	1.003	-0.075	4. %	-0.01	-0.21%
		=	CHAN. 7	QUARTZ	32-37	34.68	35.25	0.981	1.7%	36.37	1.69	7.89%
		=	CHAN. 8	TEF.PREWGD		33.90	34.75	0.981	7.78 \$	35.88	 8.	5.85%
		=	CHAN. 9F	TEFLON	32-37	33.90	34.73	0.981	1.724	35.88	2.8	5.85%
		=	CHAN. 98	QUARTZ	32-37	33.90	¥.3	0.981	1.794	35.88	1.8	5.85%
		=	CHAN.10	QUARTZ	32-37	33.90	K.	0.981	1.7%	35.88	8	5.85%
		=	CHAN.11	TEF.PREMGD	32-37	34.68	35.50	0.981	1.794	36.62	3.	5.59%
		=	CHAN.12	TEFLON	32-37	35.99	37.00	0.981	1.794	38.09	2.10	5.84%
		=		DENUDER	3-5		3.90					
HAWTHORNE 07/10/87	78/01/70	SCAQS	CHAN. 1	NATON	9-13	10.10	10.45	0.955	0.206	10.19	0.0	0.85%
		=	CHAN. 2F	ZFLOUR	20-25	22.10	22.45	1.026	-0.207	22.83	0.73	3.29%
		=	CHAN. 2B	CARBONATE	20-25	22.10	22.45	1.026	-0.207	22.83	0.73	3.29%
		=	CHAN. 3	NATON	8-10	8.30	8.55	0.955	0.206	8.37	0.07	0.86%
		=	CHAN. 4	NATON	8-10	8.80	9.25	0.955	0.206	5. 6.	0.24	2.72%
		=	CHAN. 5	OXALIC ACD	3-5	4.30	7.40	0.955	0.206	4.41	0.11	2.51%
		=	CHAN. 6	POLYCARB.	9-4	4.70	4.78	0.955	0.206	4.77	0.07	1.51%
		=	CHAN. 7		32-37	33.40	34.10	1.026	-0.207	34.78	1.38	4.13%
		=	CHAN. 8	-	32-37	32.90	34.00	1.026	-0.207	34.68	1.78	2.40%
		=	CHAN. 9F		32-37	32.60	33.80	1.026	-0.207	34.47	1.87	5.74%
		=	CHAN. 98	QUARTZ	32-37	32.60	33.80	1.026	-0.207	34.47	1.87	5.74%
		=	CHAN.10	QUARTZ	32-37	33.20	34.00	1.026	-0.207	34.68	1.48	4.45%
		=	CHAN.11	TEF.PREWGD	32-37	34.00	35.40	1.026	-0.207	36.11	2.11	6.22%
		600 600	CHAN.12	TEFLON	32-37	35,10	36.00	1.026	-0.207	36.73	1.63	4.64%
		=		DENUDER	3-5							

TABLE 5-2 (CONTINUED)

SCAGS SAMPLER FLOW AUDIT RESULTS

					SCAGMD						
			_	HOMINAL	AUDIT	ROTAMETER			≥		DELTA
SITE DATE	SAMPLER	SAMPLER 1D	D TYPE	FLOW	FLOW	READ ING	SLOPE	INTERC.	FL04	DELTA	PERCENT
1 CMG BEACH 07/31/87	7 SCAOS	CHAN. 1	NALON	9-13	10.60	10.00	0.967	0.124	8.0	-0.81	-7.60%
		CHAN. 2F		20-25	22.10	20.00	0.995	1.427	21.33	-0.77	-3.50%
	=	CHAN. 28	ပ	20-25	22.10	20.00	0.995	1.427	21.33	-0.77	-3.50%
	=	CHAN. 3		8-10	8.90	9.18	0.967	0.124	9.00	0.10	1.14%
	=	CHAN. 4		8-10	8.90	8.95	0.967	0.124	8.73	-0.15	-1.69%
	=	CHAN. 5	OXALIC ACD	3-5	4.10	4.30	0.967	0.124	4.28	0.18	4.44%
	=	CHAN. 6		9-7	4.70	4.73	0.967	0.124	4.72	0.05	0.37%
	=	CHAN. 7		32-37	36.90	34.50	0.995	1.427	35.75	-1.15	-3.10%
	=	CHAN. 8	-	32-37	36.40	34.50	0.995	1.427	35.75	-0.65	-1.77
	=	CHAN. 9F	: TEFLON	32-37	35.10	33.50	0.995	1.427	34.76	-0.34	-0.97%
	=	CHAN. 98		32-37	35.10	33.50	0.995	1.427	34.76	-0.3¢	-0.97%
	=	CHAN. 10		32-37	36.10	34.00	0.995	1.427	35.26	-0.8 8.0	-2.34%
	=	CHAN.11	-	32-37	36.10	34.50	0.995	1.427	35.75	-0.35	-0.96%
	=	CHAN. 12		32-37	36.90	35.50	0.995	1.427	36.73	-0.15	-0.41%
	=		DENUDER	3-5							
78/00/11 11/00/87	30473 21	CHAN	Z IAN	9-13	9,93	8.7	0.959	0.197	9.55	-0.38	-3.85%
LONG BEACH 11/07/0		CHAN. 2F		20-25	25.24	22.50	1.064	-1.692	22.25	-2.99	-11.85%
	=	CHAN. 28	ပ	20-25	25.24	22.50	1.064	-1.692	22.25	-2.99	-11.85%
	=	CHAN. 3	NATON	8-10	8.09	8.45	0.959	0.197	8.30	0.21	2.60%
	=	CHAN. 4		8-10	8.13	8.55	0.959	0.197	8.40	0.27	3.28%
	=	CHAN. 5	0	3-5	4.12	4.25	0.959	0.197	4.27	0.15	3.71%
	=	CHAN. 6		9-7	5.08	5.20	0.959	0.197	5.18	0.10	2.04%
	2	CHAN. 7	QUARTZ		36.52	34.25	1.064	-1.692	34.75	-1.77	-4.85%
	=	CHAN. 8	TEF.PREWGD		37.30	34.75	1.064	-1.692	35.28	-2.02	-5.41%
	=	CHAN. 9F	F TEFLON		35.99	34.00	1.064	-1.692	34.48	-1.51	-4.18%
	=	CHAN. 98		32-37	35.99	34.00	1.064	-1.692	34 48	-1.51	-4.18%
	=	CHAN. 10	QUARTZ	32-37	36.52	34.00	1.064	-1.692	34.48	-2.04	-5.58%
	=	CHAN. 11	-	32-37	35.99	34.25	1.064	-1.692	34.73	-1.24	-3.45%
	=	CHAN.12	TEFLON	32-37	38.35	36.25	1.064	-1.692	36.88	-1.47	-3.84%
	=		DENUBER	3-5							

TABLE 5-2 (CONTINUED)

SCAQS SAMPLER FLOW AUDIT RESULTS

						SCAGMD	1			:		i
					NOMINAL	AUDI	KOIAMEIEK			À		DELIA
SITE	DATE	SAMPLER	SAMPLER 10	D TYPE	FL04	FLO4	READING	SLOPE	INTERC.	FLON	DELTA	PERCENT
RUBIDOUX	07/24/87	SCAOS	CHAN. 1	NALON	9-13	10.10	11.00	0.987	-0.087	10.77	0.67	6.63%
		=	CHAN. 2F	ZFLOUR	20-25	20.20	19.73	0.971	1.666	20.84	9. 8	3.18%
		=	CHAN. 28	CARBONATE		20.20	19.75	0.971	1.666	20.84	9.0	3.18%
		=	CHAN. 3	NALON		8.50	8.8	0.987	-0.087	8.73	0.25	2.90%
		=	CHAN. 4	NATOM		8.40	8.80	0.987	-0.087	8.60	0.20	2.36%
		=	CHAN. 5	OXALIC ACD		4.00	4.20	0.987	-0.087	7.08	0.06	1.46%
		Ξ	CHAN. 6	POLYCARB.		4.50	4.73	0.987	-0.087	4.55	0.05	1.15%
		=	CHAN. 7	QUARTZ		35.10	34.25	0.971	1.666	34.95	-0.18	-0.50%
		=	CHAN. 8	TEF.PREWGD		35.90	35.25	0.971	1.666	35.89	-0.01	-0.02%
		=	CHAN. 9F	TEFLON		34.20	33.75	0.971	1.666	34.44	0.24	0.69%
		=	CHAN. 98	QUARTZ		34.20	33.75	0.971	î.666	34.44	0.24	0.69%
		=	CHAN.10	QUARTZ		35.60	35.00	0.971	1.666	35.65	0.05	0.14%
		=	CHAN.11	TEF.PREWGD		35.60	35.00	0.971	1.666	35.65	0.05	0.14%
		=	CHAN . 12	TEFLOW		35.10	34.00	0.971	1.666	34.68	-0.45	-1.20%
				DENUDER								
SAN N.1S. 07/21/87	07/21/87	SCAQS	CHAN. 1	NATION	9-13	9.87	11.00	0.947	0.150	10.57	0.70	7.06%
		=	CHAN. 2F	ZFLOUR	20-25	22.38	23.00	0.983	0.150	22.76	0.38	1.69%
		=	CHAN. 28	CARBONATE	20-25	22.38	23.00	0.983	0.150	22.76	0.38	1.69%
		=	CHAN. 3	NATON	8-10	8.47	8.80	0.947	0.150	8.48	0.01	0.16%
		=	CHAN. 4	NATON	8-10	8.34	9.6	0.947	0.150	8.67	0.33	3.9%
		=	CHAN. 5	OXALIC ACD	3-5	4.21	4.30	0.947	0.150	4.22	0.01	0.29%
		=	CHAN. 6	POLYCARB.	9-4	4.76	4.80	0.947	0.150	4.70	-0.06	-1.35%
		=	CHAN. 7	QUARTZ	32-37	33.71	34.65	0.983	0.150	34.21	0.50	1.49%
		=	CHAN. 8	TEF.PREWGD	32-37	33.44	34.80	0.983	0.150	34.36	0.92	2.75%
		=	CHAN. 9F		32-37	34.25	35.00	0.983	0.150	34.56	0.30	0.89%
		=	CHAN. 98	QUARTZ	32-37	34.25	35.00	0.983	0.150	34.56	0.30	0.89%
		=	CHAN. 10	QUARTZ	32-37	33.98	35.00	0.983	0.150	34.56	0.58	1.69%
		=	CHAN.11	TEF.PREWGD	32-37	35.06	36.00	0.983	0.150	35.54	0.48	1.36%
		=	CHAN. 12	TEFLON	32-37	34.79	35.50	0.983	0.150	35.05	0.26	0.74%
		=		DENUDER	3-5							

TABLE 5-3

SUMMARY OF SCAQS SAMPLER FLOW AUDITS

SNI 07/21	7 1	•	1.7	1.7	0.5	4.0	0.3	-1.4	1.5	2.8		٠. د د	0.0	1.7	1.4	7	•
RUB 07/24	9 9	•	3.5	3.2	2.9	2.4	1.5	1.2	-0.5	0	•		0.7	0.1	0.1	,	7.1
LB 11/09	0 %	0.0	-11.9	-11.9	5.6	3.3	3.7	2.0	-4.9	15 A	•	-4.2	-4.2	-5.6	-3.5	0	0.5
LB 07/31	7 6	0./1	-3.5	-3.5	1.1	-1.7	4.4	0.4	-3.1	α .) · ·	-1.0	-1.0	-2.3	-1.0	•	10.
HAW 07/10																	
DLA 11/09	1.1	11.0	1.8	1.8	4.1	4.0	-0.4	-0.2	4.9		U .	5.9	5. 0	5.9	5.6		ν. Ω
DLA 07/10																	
BUR 07/01	0	7.8	0.0-	0.0-	4.8	5.6	4.7	3.7	٠, ١	4 -	L. 3	1.4	1.4	2.0	2.4		3.1
AZU 07/01	,	8.9	12.5	12.5	5.0	8,0	11.9	9,0	2		7.7	3,3	3.3	2.7	3.0	3 ·	1.6
ANA 07/24		ი ი.	0.0	0.0	8.0-	0	3.1	ι α 	• • • • • • • • • • • • • • • • • • •	* ·	0.2	-0.7	-0.7	-1.4	1	•	-0.7
NOMINAL FLOW		9-13	20-25	20-25	8-10	8-10) 1 1 1 1	7 4	7 7 7	75-25	32-37	32-37	32-37	32-37	22-27	16-36	32-37
CHANNEL		NATON	ZFT.OITR	2R CARRONATE	NOTAN	NOTAN	CON CITY	OATUCA BCD	OII CAND.	QUAKT'S	LEF. PREWGD	TEFLON	OIIARTZ	OITA P.T.		LEF . FRENGE	TEFLON
CHA		Н	고	2 H	, 1 4 6) <	ט ד	י ה	4 0 t	•	8	9 F	86	, ר ני	ב זר	7.7	12
												5.	- a				

Carbonyl Sampler

Results for audits of the carbonyl sampler flow rates are shown in Table 5-4. Results are within reasonable expectations for this sampler, except for the 22 percent difference at Anaheim during the summer study. Also, the ENSR flow rates on average are biased lower than the audit flow rates. These discrepancies have not been resolved, nor have the audit values been incorporated into the calculation of carbonyl concentration.

Aerosol Particle Counters, Impactors and Cyclones

The results of flow rate audits on aerosol particle counters and impactors are shown in Table 5-5.

The results for the EAA and OPC particle counters show reasonable agreement between instrument design flow rates and audit flow rates. However, the results for the PMS Probe showed extreme bias and were discounted. The SCAQMD TSD reported that the PMS Probe flow rates were too low to be accurately audited with the equipment employed during the summer audits. The discrepancy for fall audit results on the Probe was never resolved. The audit results were not reported until after the audit visit, and thus discrepancies could not be discovered and resolved onsite.

Audit results for the MOUDI and Berner impactors showed good agreement with design flow rates. September flow rate audit results for the DRUM Impactor showed such extreme and consistent bias that the audit results were discounted. No probable explanation for the discrepancy has been identified. Audit results were not reported until well after the audit, and thus it was not possible to discover and investigate these discrepancies onsite. However, the University of California, Davis (UCD) had checked the DRUM calibrations onsite before and after the study. During the fall audit, the DRUM audit flow rates were in good agreement with the design flow rates.

TABLE 5-4
CARBONYL FLOW RATE AUDIT RESULTS

SITE	DATE	ENSR FLOW LPM	AUDIT FLOW LPM	DIFF.	DIFF. PERCENT
Anaheim Azusa Burbank Claremont Hawthorne Rubidoux San Nicolas Is.	07/24/87 07/01/87 07/01/87 08/06/87 07/10/87 07/24/87 07/21/87	1.06 0.81 1.03 0.82 0.96 0.92 0.93	1.37 0.85 1.00 0.77 1.10 1.00	-0.31 -0.04 0.03 0.05 -0.14 -0.08 -0.09	-22.6% -4.7% 3.0% 6.5% -12.7% -8.0% -8.8%
Anaheim Burbank DOLA Hawthorne Long Beach Rubidoux	12/22/87 12/15/87 11/09/87 12/15/87 11/09/87 12/22/87	1.10 1.01 0.89 0.91 0.84 1.05	1.15 1.05 0.92 1.02 0.92 1.08	-0.05 -0.04 -0.03 -0.11 -0.08 -0.03	-4.3% -3.8% -3.3% -10.8% -8.7% -2.8%

TABLE 5-5

FLOW RATE AUDIT RESULTS FOR
AEROSOL PARTICLE COUNTERS, CYCLONES, AND IMPACTORS

Site	<u>Date</u>	Instrument Flow	Design Flow (lpm)	Audit Flow (lpm)	Difference From Design (%)
Long Beach	07/31	EAA Aerosol	4.0	4.5	12.5
Rubidoux	08/03	EAA Aerosol	4.0	4.2	5.0
Claremont	08/06	EAA Aerosol	4.0	4.63	15.8
Dola	11/09	EAA Aerosol	4.0	4.21	5.3
Long Beach	11/09	EAA Aerosol	4.0	4.57	14.3
Long Beach	07/31	EAA Total	54.0	55.4	2.6
Rubidoux	08/03	EAA Total	54.0	54.1	0.2
Claremont	08/06	EAA Total	54.0	53.4	1.1
Long Beach	07/31	OPC	7.0	6.8	- 2.9
Rubidoux	08/03	OPC	7.0	6.8	- 2.9
Claremont	08/06	OPC	7.0	6.46	- 7.7
Long Beach	11/09	OPC	7.0	6.51	- 7.0
Long Beach	07/31	Probe	0.06	0.16	a
Rubidoux	08/03	Probe	0.06	0.16	a
Claremont	08/06	Probe	0.06	0.16	a
Dola	11/09	Probe	0.06	17.44	a
Long Beach	11/09	Probe	0.06	16.52	а
Claremont	09/04	MOUDI	30.0	30.2	0.7
Rubidoux	09/04	MOUDI	30.0	31.8	6.0
Dola	11/09	MOUDI	30.0	30.2	0.7
Long Beach	11/09	MOUDI	30.0	30.2	0.7
Claremont	09/04	Berner	30.0	30.2	0.7
Rubidoux	09/04	Berner	30.0	30.5	1.7
Dola	11/09	'Berner	30.0	28.7	- 4.3
Long Beach	11/09	Berner	30.0	28.1	- 6.3
Claremont	09/04	DRUM	1.0	0.22	а
Long Beach	09/04	DRUM	1.0	0.22	a
Rubidoux	09/04	DRUM	1.0	0.22	a
Dola	11/09	DRUM	1.0	1.09	9.0
Long Beach	11/09	DRUM	1.0	1.03	3.0

^a Audit values are suspect. Subsequent investigations indicate that it is extremely unlikely that audit values are correct as reported.

Audit results for the AIHL and Sensidyne cyclones showed good agreement with design flow rates.

SSI PM₁₀ Hivols

The SCAQMD TSD calibrated SSI Hivols at Claremont and Long Beach on 6/12/87. The ARB QA Section audited Hivol and SSI Hivol flow rates at Claremont and Downtown Los Angeles on 6/18/87 and 6/16/87, respectively. All results were within 5 percent.

5.3 Nephelometer Audits

The SCAQMD TSD audited the nephelometers installed and maintained by AV at the SCAQS B- and B+-sites. The nephelometers were MRI Model 1560 series adjusted to measure zero for Rayleigh scattering of pure air, and thus measured particle scattering directly. The instruments were spanned by AV with freon-22 and freon-12 to read 0.88 and 1.92 per 10⁻⁴m⁻¹ meters, respectively. AV checked the nephelometers between each intensive period and adjusted them if necessary.

The auditor challenged the instrument with Freon-12. The results are shown in Table 5-6. The results are generally good except at Rubidoux. In this case, the instrument response was noisy, probably due to dust in the light chamber. AV's frequent calibration checks show occasional problems such as that which occurred at Rubidoux during the audit. These occasional problems were routinely caught and corrected between intensive study days.

5.4 Continuous Gas Analyzer Audits

The ARB QA Section conducted audits for the continuous gas analyzers at the SCAQS A and B sites, and those mounted in the STI and UW aircraft. As discussed below, the audits identified a number of problems. To help resolve these problems, calibration

TABLE 5-6

NEPHELOMETER AUDIT RESULTS

site	Date	Reference Response /1000 m	F-12 Response /1000 m	Zero Response /1000 m	Net Response /1000 m	Diff. (%)
Anaheim	07/24/87	1.92	1.87	0.03	1.84	- 4.2
Azusa	07/23/87	1.92	1.86	00.0 -	1.86	- 3.1
Burbank	07/27/87	1.92	Noisy	0.07	1	!
Claremont	07/23/87	1.92	1.98	90.0	1.92	0°0
DOLA	07/27/87	1.92	1.96	0.09	1.87	- 2.6
Hawthorne	07/27/87	1.92	1.76	- 0.01	1.77	- 7.8
Long Beach	07/24/87	1.92	2.00	0.02	1.98	3.1
Rubidoux	07/24/87	1.92	2.44ª	0.16^{a}	2.28	18.8

a Noisy response.

checks were also provided by ARB Haagen-Smit Laboratories, by SCAQMD, and by STI. The results of the gas analyzer audits are shown in Table 5-7, grouped by monitoring organization.

SCAOMD Sites

The monitoring sites operated by the SCAQMD are audited annually by the SCAQMD QA Section to meet EPA requirements. In addition, a sample of stations is audited by the ARB QA Section each year as a cross check. ENSR reviewed the ARB audit data for 1985, 1986, and 1987, and found generally very good results. Since the SCAQMD sites are ongoing operations with a history of good audit results, the performance audit efforts for SCAQS were focused on the A-sites and the aircraft.

Time was available to audit one SCAQMD site, Los Angeles - North Main, referred to as Downtown Los Angeles (DOLA) during the study. Results for this site were very good during both the summer and fall audits.

General Motors Van

The GM Van was operated at Claremont during the summer study and at Long Beach during the fall. The first audit at Claremont showed good results for O_3 , but poor results for NO_2 , SO_2 , CO, and THC. The poor results were confirmed by a second audit a few days later and again by Haagen-Smit Laboratory. The differences were eventually traced to problems with the calibration system, that were subsequently corrected by GM. Later audits of the GM van at Claremont by the SCAQMD and at Long Beach by the ARB QA Section showed good results for NO_2 and CO.

The early data, collected by GM during the period of faulty calibration, have since been corrected to reflect the best available estimates of calibration values. Applying these

TABLE 5-7

GAS ANALYZER PERFORMANCE AUDIT RESULTS

CH4	audit site value value diff ppb ppb %	.9 18.0 6.5 .8 7.4 8.8 avg diff 7.7	avg diff 4.3					
	diff	2.4 16 -2.9 6 -0.3	% 0.9	39.1				
	audit site value value ppmppm_	16.9 17.3 6.8 6.6 avg diff	avg diff	4.5 6.3 avg diff				
	diff	-6.3 -3.7 -3.3	3.4	-22.4	-24.4 -26.8 -25.6			
S02	audit site value value pob pob	399 374 188 181 76 76 avg diff	avg diff	49 38 avg diff	78 59 41 30 avg diff			
	diff	-9.2 -10.9 -2.9 -7.6	1.4	-35.1 -33.8 -34.5	-26.9 -26.6 -26.7	-35.9 -38.6 -43.5 -44.6	-2.8 -4.1 -4.5	-0.6
	audit site value value pob pob	390 354 175 156 70 68 avg diff	avg diff	174 113 65 43 avg diff	175 128 64 47 avg diff	0 1 410 263 233 143 116 65 56 31 avg diff	0 0 216 210 160 154 98 94 28 26 avg diff	180 179 72 71 avg diff
	diff	3.1 3.4 17.6 17.6 17.6 17.6 17.6 17.6 17.6 17.6	6.4		-64.1 17 -50.8 6	2854	-10.9 -10.0 -9.5 -9.9	.4.1 18 .2.7 .1.
	audit site value value <u>pom</u> pom	38.6 39.8 18.2 19.1 7.4 7.8 avg diff	avg diff	not ready	38.7 13.9 19.5 9.6 avg diff		45.0 40.1 40.0 35.9 20.0 27.0 20.0 18.1 10.0 9.1 avg diff.	39.5 37.9 18.6 18.1 6.6 6.7 avg diff
	diff	-2.9 -2.8 -3.4	6.6-	.3.0 -5.1 -4.5				
വ	t site value <u>pob</u>	7 395 10 175 14 70 avg diff	avg diff	388 76 167 74 70 avg diff				
	audit value 	3 2 7	1	357	37	CLARE 7/3/87 GM Audit of NOX not NO2 by Haagen Smit	37 and	787
	DATE	6/16/87	11/19/87	6/18/87	6/27/87	7/3/87 of NOX no agen Smit	CLARE 9/4/87 GM Audit of CO and NO2 by SCAGMD	11/17/87
	S1TE GROUP	DOLA SCACHD	SCAGHD	CLARE GM	CLARE GM	CLARE GM Audit by Haa	CLARE GM Audit NO2 by	

TABLE 5-7 (CONTINUED)

GAS ANALYZER PERFORMANCE AUDIT RESULTS

audit site	value value diff													
THC audit site	value value diff													
	diff	20.9 30.8 25.5	46.4 20.6 16.9 28.0	0.0			43.2	43.2	48.4 35.6 62.5	48.8	131.1	186.7	23.2	172.1
502	value	480 236 102 diff	563 217 76 diff	3 3	<u> </u>		23	avg diff	138 19 05	di ff	50 50	38:	2	avg diff
	value pop	397 189 78 avg	384 180 65 avg	r	57 ≱8		7,7	avg	55 2 5	avg	59 %	9 R 5	ნ	avg
	diff	-4.9 -5.2 -12.7 -7.6	10.9 10.2 10.4	-7.5	C: 2:	0.01	78.0 112.5	8.3	81.2 84.8	83.0	116.3	8.85 2.1.1	%	109.1
NO2	value ppb	369 163 48 diff	418 194 77 diff	371	E	avg diff	292 68	diff	308 122	di ff	530	540	120	di ff
1	value	388 172 55 avg	377 418 176 194 70 77 avg diff	233	55 Ag	avg	2 22	avg	170 86	avg	245	₹ £2 :	19	avg
	dift *	0.8 9.3 -5.7	-0.5 -4.5 -2.2				-3.4 -3.4 0.0	-2.2						
8	value pom	38.7 16.6 7.0 diff	38.9 18.0 6.3 diff				37.2 17.3 4.3							
1	value ppm	38.4 18.3 7.5 avg	39.1 18.3 6.6 avg				38.5 17.9	9/8						
	diff	-3.7 -4.6 -4.6	6.1. 0.01. 0.01.	.3.5 -2.4.2 -2.9	 	12.7	4.3 75.4	39.9	93.8 80.8 7	88.5	104.3	132.0	120.3 103.1	119.2
8	site value ppb	02 387 74 166 74 70 avg diff	38 27 38 57 57 57	381 158 68	avg diff	avg diff	168 107	avg diff	35.8	diff	525	38	<u>ড</u>	avg diff
	audit value pob	402 174 74 avg	397 180 72 avg	395 165 05			161 61	1	5 8 7	avg			35 26	avg
	date	6/17/87	11/17/87	AIRCRAFT 6/22/87 STI	AIRCRAFT 11/15/87		AIRCRAFT 6/23/87 UM		AIRCRAFT 6/26/87 UM		AIRCRAFT 7/27/87	of NOX	2. Audit	
	Si te Group	L.B. ARB	L.B. ARB	AIRCRA STI	AIRCRA	<u>.</u>	AI RCRA UN		AI RCRA UN		AIRCRA	UW Audit of	not M02. by ST1.	: 1

recalibrations to the audit data led to good agreement with audit concentrations.

ARB Haagen-Smit Laboratory

Audits at the ARB Haagen-Smit site in Long Beach show good results for O_3 , CO, and NO_2 , but a consistent bias for SO_2 . These results hold true during both summer and fall audits. The discrepancy for SO_2 was traced to a problem with the calibration span gas and the data have been corrected to reflect the correct span values.

Sonoma Technology Aircraft

The audit results for the STI Aircraft are within the ARB tolerance limits of 15 percent for average percent difference. However, there are moderate discrepancies. STI investigated the discrepancies and confirmed the existing calibrations. The source of the discrepancies could not be determined.

University of Washington Aircraft

Audits of the UW aircraft showed problems for O_3 , NO_2 , and SO_2 . A follow-up audit by the ARB QA section and a calibration check by STI confirmed the problems. UW investigated the calibrations and resolved all discrepancies. The following explanations are discussed more fully in Hegg and Hobbs (1988).

For NO_2 , an error in permeation tube calculations was corrected, and the calibration range was extended. UW reports that after these adjustments were made, the audit differences for NO_2 were less than 10 percent.

For SO_2 , repeated gravimetric determinations of calibrator permeation rate demonstrated that the permeation rate was erratic. The value used to calibrate for the SCAQS study was changed to a value measured during the study. UW reports that after this

adjustment, the audit differences for SO_2 were less than 12 percent.

For O_3 , the audit difference was traced to an erroneously calibrated O_3 generator. The O_3 generator was then calibrated against a secondary standard calibrated by the Department of Energy (DOE). UW reports that after applying the new calibration data to the audit data, the audit differences were less than 10 percent.

5.5 Meteorological Audits

The ARB QA Section performed simple checks on meteorological instrumentation. These audits were not intended to provide precise quantitative data. Instead, they were intended to detect major malfunctions and misadjustments, such as a wind direction sensor 180 degrees out of alignment. Wind direction was checked with a hand-held compass, wind speed was checked with a hand-held anemometer, temperature with a traceable thermometer, and humidity with a battery-operated psychrometer. The audit results are shown in Table 5-8. These results show that all instruments were functioning well.

Small to moderate biases were observed for wind speed, wind The auditor noted that audit direction, and temperature. temperature readings at several sites were probably high, since they were taken approximately 5 feet above surfaces such as hot asphalt roofs rather than at tower height. Wind direction averages about 10 degrees lower than audit values (i.e. station north points This may reflect a discrepancy in east of audit true north). magnetic corrections, which are about 15 degrees. The bias in wind speed has been explored. This comparison is based on the auditor visually averaging the station response and the audit device response to varying wind speeds, and does not warrant quantitative conclusions. It appears that if the audit device were reading miles per hour instead of knots, the bias might be reduced. audit device is able to read in knots, miles per hour, or meters

TABLE 5-8
PERFORMANCE AUDIT RESULTS FOR WETEOROLOGICAL MEASUREMENTS

KLK 9/17/87 HUMIDITY/DEW POINT

SITE CHECK

RESPONSE DEVICE

30x 29x 56

52 56

52 55

54.8 57 57.1 TEMPERATURE

DEGREES CELSIUS
SITE CHECK
RESPONSE DEVICE
25.2 25.6
25.9 27.2
25.3 29.4
25.3 29.4
26.2 21.1
31.6 31.5 CHECK DEVICE 7'5 4'5 6'6 4'5 WIND SPEED KNOTS SITE RESPONSE CLAREMONT MCKENNA ANAHEIM BURBANK AZUSA HAWIHORNE SONOMA TECHNOLOGY NG670Y RUBIDOUX SITE

Blanks Indicate no Instrument

per second. The auditor states that he recorded audit device readings as knots. The possibility of a mixup exists, but cannot be confirmed.

6. SPECIAL STUDIES AND INTERCOMPARISONS

6.1 Nitrogen and Carbonaceous Species Methods Comparison Studies

Two comprehensive field and laboratory comparison studies, the Nitrogen Species Methods Comparison Study (NSMCS) and the Carbonaceous Species Methods Comparison Study (CSMCS), were coordinated by ARB to facilitate the planning for SCAQS. The objectives of the studies were to quantify differences among sampling methods and to assess the magnitude of specific types of sampling artifacts.

The NSMCS was conducted in September 1985 at Pomona College in Claremont, California. Its main objective was to evaluate methods for sampling nitric acid and other nitrogenous pollutants such as ammonia, nitrous acid, and nitrogen dioxide during SCAQS (Lawson, et al. 1988). Results from the NSMCS showed that the diffusion denuder method and diffusion tube, two routine monitoring methods, were nearly equivalent to spectroscopic methods for the measurement of nitric acid and ammonia, respectively. Results were inconclusive for the other species, so redundant measurements using a variety of techniques were included in SCAQS.

The CSMCS was conducted in August 1986 at Citrus College in Glendora, California. The objectives were to evaluate analytical methods for measurement of total "organic" and "elemental" carbon on a suite of 20 separate samples by means of an interlaboratory round robin (Hering 1988). Regression analyses performed by ARB staff (Lawson 1989a) showed that the carbon analysis method employed by ENSR was closest to the mean of all the methods for the three carbon components. Inasmuch as no NBS-traceable standards are available for total "organic" and "elemental" carbon particles, the Coordinating Research Council (CRC), upon recommendation from ARB, decided to fund ENSR to provide analysis of the SCAQS sampler filters for carbon.

During the CSMCS, a formaldehyde methods evaluation study was carried out (Lawson, et al. 1989b) in order to evaluate formaldehyde measurement techniques. The Fourier transform infrared (FTIR), differential optical absorption spectroscopy (DOAS), tunable diode laser absorption spectrometer (TDLAS), diffusion scrubber, enzymatic method, and dinitrophenolhydrazine (DNPH) cartridges were evaluated, and the DNPH method was chosen. All reported values averaged less than 20 percent from the mean of the three spectroscopic methods (FTIR, DOAS, and TDLAS).

A hydrogen peroxide sampling methods evaluation was also conducted during the CSMCS (Lawson 1989c). The TDLAS, diffusion scrubber, impinger, enzymatic technique, and cold trap U-tube were evaluated, and considerable difference among methods was shown. The difference among methods was greater than the experimental error of the methods, with no conclusion regarding a method which would be accurate and suitable for routine measurement of $\rm H_2O_2$ during SCAQS. However, after considerable evaluation by ARB and staff and CRC members, CRC chose to fund the TDLAS and impinger methods for $\rm H_2O_2$ measurement during SCAQS. Both the formaldehyde and hydrogen peroxide evaluations were conducted without the use of suitable reference standards.

Evaluation of sampling and analytical methods in NSMCS and CSMCS served as an initial phase of QA for SCAQS.

6.2 Precision Test of SCAQS Sampler

Prior to the field study, AV operated all ten SCAQS samplers sideby-side to verify equivalency and to determine precision of results. The sampling was conducted between June 3 and June 7, 1987 at the AV facility in Monrovia. Pollutant concentrations were unusually low during the evaluation, resulting in loadings near or below detection limits for low flow filters. When the loadings were sufficiently above the overall detection limit, the coefficients of variation were between 5 percent and 10 percent. For very low loadings, the coefficients of variation were generally less than the percent overall detection limits. The details of the precision tests and results are documented in a report prepared by Fitz and Savicker (1988).

6.3 SCAQS Comparison Studies

In addition to the performance audits described in Sections 4 and 5, ARB coordinated comparison studies for elemental analysis, speciated hydrocarbons, light absorption and PAN due to the difficulty of defining performance audit procedures for these measurements. The results of the comparison studies are summarized below. Data submitted by each participating laboratory are compiled in Appendices B, C, D, E, and F.

6.3.1 Elemental Analysis

Sixteen Teflon filters (two duplicate sets of three PM, and three PM₁₀ samples plus two duplicate sets of one PM₂₅ and one PM₁₀ field blanks) were analyzed by wavelength dispersive XRF at EPA/NSI (SCAQS laboratory), NEA, Inc., and the Monitoring and Laboratory The collocated samples were collected with the Division of ARB. prototype SCAQS aerosol sampler in Monrovia, California between March 26, 1987 and April 8, 1987. One sample from each pair was later analyzed by wavelength dispersive XRF at Desert Research Institute (DRI) followed by Instrumental Neutron Activation Analysis (INAA) at the University of Maryland. Five of the second set of filters were analyzed by particle induced x-ray emission (PIXE) at UCD. A set of eight single elements (aluminum, silicon, potassium, calcium, vanadium, iron, copper, and lead) Micromatter standards and two multi-element NBS standards were analyzed by NSI. The SRMs were previously analyzed by DRI as part of QA for the Denver Brown Cloud Study.

Results of analysis of XRF SRMs by NSI were in excellent agreement with the reference values (Table 6-1). With one exception, the differences were within 10 percent of the reference values.

The scatter diagrams in Figure 6-1 show that NEA obtained higher values than EPA/NSI for soil related elements in coarse particles, while excellent agreement was obtained for sulfur which is found mostly in fine particles. Similar differences were found between ARB and EPA/NSI. Sample nonuniformity was suspected as the cause since a 1-cm² area in the center of the filter is exposed by both NEA and ARB while nearly the entire deposit area (3-cm diameter) is exposed by NSI. Visual evidence of nonuniformity was reported by DRI in samples collected with the SCAQS Sampler (Chow 1988).

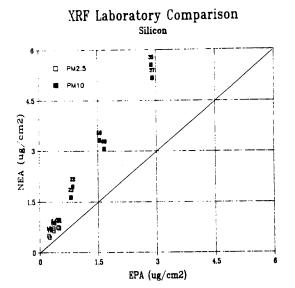
In order to investigate the degree of nonuniformity, five of the comparison samples were sent to UCD and scanned by PIXE edge-toedge to establish the element-specific gradients. The PIXE scan shown in Figure 6-2 confirms that particles collected with the SCAQS Sampler, as originally designed, are not uniformly deposited. A limited comparison of NSI's XRF results with the average of the PIXE scans showed good agreement in some cases but differences in These comparisons show that the large area of exposure used by NSI will average out much of the spatial inhomogeneity in However, the result may not be the true average the sample. because the x-ray beam intensity is not uniform (Kellogg 1989). In order to investigate this question, six of the comparison samples were analyzed by INAA at the University of Maryland, and the results were compared to the XRF analyses. The comparisons for NSI's values for iron and aluminum are shown in Table 6-2. aluminum are generally in good agreement with the INAA data while iron values are consistently higher by 16 to 37 percent for PM25 and by 42 to 59 percent for PM_{10} . Uncertainties in the data were high for the other elements due to concentrations near or below detection limits and relatively high blank values.

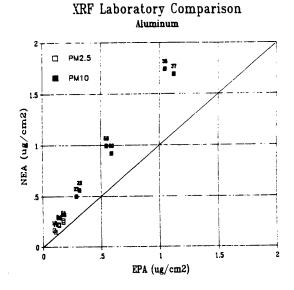
1200-004-001

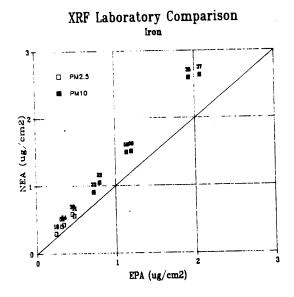
TABLE 6-1

ANALYSIS OF STANDARD REFERENCE MATERIALS FOR XRF NSI

Aluminum Aluminum 14.26 .95 15.13 .80 .87 6.1 Aluminum 33.27 1.11 31.79 1.63 -1.48 -4.4 Calcium 19.01 1.27 19.30 .97 -29 1.4 Vanadium 4.60 .48 4.18 .23 42 -9.1 Manganese 4.44 .48 4.87 .39 43 -9.1 Cobper 2.38 1.00 .16 .97 .07 03 -9.4 NBS 113con 1.6.98 1.6 .15 .15 .15 03 -9.4 Silicon 16.98 1.67 15.99 .80 17 20 8.4 Zinc 1.69 1.67 1.59 -1.17 20 5.8 Zinc 1.60 1.67 1.59 -1.17 -1.1 20 5.1 Aluminum 1.6.22 1.76 1.78 1.78 -1.78 -1.78	XRF SRMS	Certified ug/cm ²	± ug/cm²	Conc. ug/cm ²	2-sigma µg/cm ²	Diff.	Diff.
33.27 1.11 31.79 1.63 -1.48 -4.4 4.60 .48 4.48 .97 .29 1.1 4.44 .48 4.87 .39 .42 -9 1.00 .06 .97 .07 03 -3 1.00 .06 .97 .07 03 -3 2.38 .16 .80 03 -3 -8 16.98 1.67 15.99 .80 99 -5 16.98 1.67 15.99 .80 99 -5 14.10 .46 14.25 .80 99 -5 14.10 .30 3.74 .21 99 -5 16.22 .76 15.13 .78 - 1.09 -6 16.22 .76 15.13 .78 - 1.73 - 1.74 - 1.75 16.22 .76 1.20 .86 1.73 - 1.74 - 1.74 - 4.4 19.00 .95 17.32 .86 - 1.74 - 1.74 - 1.74	1832-1 Luminum	4	6	5.1	Φ	8	•
19.01 1.27 19.30 .97 .29 .29 .29 .29 .99 .29 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .99 .90 .99 .99 .90 .99 .90 .99 .90 .99 .90 .99 .90 .99 .90 .99 .90 .99 .90 .99 .99 .90 .99 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90 .90	ilicon	ж Э	۲.	1.7	•	1.4	4.
4.60 .48 4.18 .23 42 -9 4.44 .48 4.87 .39 .43 9 1.00 .06 .97 .07 03 -3 2.38 .16 .80 99 8 8 16.98 1.67 15.99 .80 99 5 12.73 1.82 13.16 .66 .43 3 14.10 .46 14.25 .75 .15 1. 3.94 .30 3.74 .21 20 5 16.22 .76 15.13 .78 -1.09 6 10.19 1.02 8.44 .43 -1.75 -17 10.19 1.80 34.26 1.73 .174 -4 19.00 .95 17.32 .86 -1.74 -4 12.32 .62 11.22 .56 -1.10 -8 2.31 1.20 12.24 .62 -1.00 -9 12.00 1.20 12.24 .62 -1.76 <t< td=""><td>Salcium</td><td>о О</td><td>7</td><td>9.3</td><td>9</td><td>2</td><td>4</td></t<>	Salcium	о О	7	9.3	9	2	4
1.00 .48 4.87 .39 .43 9. 1.00 .06 .97 .07 03 -3. 2.38 .16 2.18 .13 03 -3. 1.00 1.67 15.99 .80 99 -5. 12.73 1.82 13.16 .66 .43 3. 16.22 .76 14.25 .75 .15 1. 16.22 .76 15.13 .78 -1.09 -6. 16.22 .76 15.13 .78 -1.09 -6. 16.22 .76 15.13 .78 -1.79 -6. 16.22 .76 15.13 .78 -1.79 -6. 16.22 .76 15.13 .86 -1.74 -4. 16.23 .85 17.13 .86 -1.74 -4. 19.00 .95 17.32 .87 -1.10 -8. 2.31 .23 .221 .11 -1.10 -8. 12.00 1.20 8.07 .41 76 </td <td>/anadium</td> <td>•</td> <td>4</td> <td>4.1</td> <td>~</td> <td>4.</td> <td>თ</td>	/anadium	•	4	4.1	~	4.	თ
1.00 .06 .97 .07 03 -3. 2.38 .16 2.18 .13 03 -8. 16.98 1.67 15.99 .80 99 -5. 12.73 1.82 13.16 .66 .43 3. 12.73 1.82 13.16 .66 .43 3. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 -6. 10.19 1.02 8.44 .43 -1.75 -17 36.00 1.80 34.26 1.72 -1.74 -4. 19.00 .95 17.32 .87 -1.16 -8. 2.31 .23 12.24 .65 -1.10 -8. 12.00 1.30 12.24 .65 -1.10 -8. 9.00 .90 8.07 .41 -93 -10.	fanganese	•	₽	φ.	ന	4	9
2.38 .16 2.18 .13 20 -8. 32.14 2.12 30.97 1.59 -1.17 -3. 16.98 1.67 15.99 .80 99 -5. 12.73 1.82 13.16 .66 99 -5. 14.10 .46 14.25 .75 .15 1. 3.94 .30 3.74 .21 99 -5. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 -1.79 -6. 10.19 1.02 8.44 .43 -1.74 -4. 19.00 .85 17.32 .86 -1.74 -4. 19.00 .95 17.32 .87 -1.68 -8. 2.31 .23 2.21 .11 -1.0 -8. 12.00 1.20 12.24 .65 -1.10 -9. 9.00 .90 8.07 .41 -9.3 -10.	cobalt	•	0	6.	0	•	س
2 32.14 2.12 30.97 1.59 -1.17 -3. 16.98 1.67 15.99 .80 99 -5. 12.73 1.82 13.16 .66 .43 3. 14.10 .46 14.25 .75 .15 1. 3.94 .30 3.74 .21 20 -5. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 -1.75 -17. 10.19 1.02 8.44 .43 -1.75 -1.7 -4. 19.00 .95 17.32 .87 -1.74 -4. 12.32 .62 11.22 .56 -1.10 -8. 13.00 1.20 12.24 .65 -1.10 -8. 12.00 .90 8.07 .41 -1.76 -5.	Copper	•	\vdash	٦.	Н	.2	ω.
32.14 2.12 30.97 1.59 -1.17 -3. 16.98 1.67 15.99 .8099 -5. 12.73 1.82 13.16 .66 .43 3. 14.10 .46 14.25 .75 .15 1. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 -1.75 .17 .17 -1.75 .17 -1.75 .17 -1.75 .17 .17 -1.75 .17 -1.75 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17	3 1833-977						
16.98 1.67 15.99 .80 99 -5. 12.73 1.82 13.16 .66 .43 3.7 14.10 .46 14.25 .75 .15 1. 3.94 .30 3.74 .21 20 -5. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 -1.75 -17. 10.19 1.02 8.44 .43 -1.75 -17. 19.00 1.80 34.26 1.72 -1.74 - 4. 19.00 .95 17.22 .56 -1.10 - 8. 2.31 .23 2.21 .11 - 1.0 - 8. 13.00 1.30 12.24 .65 - 7.76 - 5. 12.00 1.20 8.07 .41 93 - 10.	ilicon	2.1	•	0.9	ហ	-	ď
12.73 1.82 13.16 .66 .43 3.74 14.10 .46 14.25 .75 .15 1.15 3.94 .30 3.74 .21 20 -5. 16.22 .76 15.13 .78 -1.09 -6. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .17 -1.75 10.19 1.80 34.26 1.72 -1.74 -4. 19.00 .95 17.32 .87 -1.68 -8. 12.32 .62 11.22 .56 -1.10 -8. 2.31 .23 2.21 .11 -10 -4. 13.00 1.20 12.24 .65 -7.76 -5. 9.00 .90 8.07 .41 93 -10.	otassium	6.9	•	5,9	φ	٠ •	2
14.10 .46 14.25 .75 .15 .15 15.13 .21 20 -5. 3.94 .30 3.74 .21 20 -5. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 -1.75 -17. 10.19 1.80 34.26 1.72 -1.74 -4. 19.00 .95 17.32 .87 -1.68 - 8. 12.32 .62 11.22 .56 -1.10 - 4. 13.00 1.30 12.24 .62 - 776 - 5. 12.00 .90 8.07 .41 - 93 -10.	litanium	2.7	•	3.1	9	4,	3
3.94 .30 3.74 .21 20 -5. 16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 -17. 10.19 1.02 8.44 .43 -1.75 -17. 36.00 1.80 34.26 1.72 -1.74 -4. 19.00 .95 17.32 .87 -1.68 - 8. 12.32 .62 11.22 .56 -1.10 - 8. 2.31 1.20 12.24 .62 76 - 5. 12.00 1.20 8.07 .41 93 -10.	ron	4.1	•	4.2	7	۳-	4
16.22 .76 15.13 .78 -1.09 -6. 17.00 .85 17.13 .86 .13 .17 10.19 1.02 8.44 .43 -1.75 -17 36.00 1.80 34.26 1.72 -1.74 -4. 19.00 .95 17.32 .87 -1.68 - 8. 12.32 .62 11.20 -1.10 - 8. 2.31 1.30 12.24 .62 10 - 4. 13.00 1.20 12.77 .65 76 - 5. 12.00 .90 8.07 .41 93 -10.	inc	6		3.7	2	.2	ري م
17.00 .85 17.13 .86 .13 .13 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 .17 <	ead	6.2		5.1	7	1.0	9
17.00 .85 17.13 .86 .13 .17 10.19 1.02 8.44 .43 -1.75 -17 36.00 1.80 34.26 1.72 -1.74 - 4. 19.00 .95 17.32 .87 -1.68 - 8. 12.32 .62 11.22 .56 -1.10 - 8. 13.00 1.30 12.24 .62 76 - 5. 12.00 1.20 12.77 .65 76 - 5. 9.00 .90 8.07 .41 93 -10.							
lm 17.00 .85 17.13 .86 .13 .17 lo.19 1.02 8.44 .43 -1.75 -17 36.00 1.80 34.26 1.72 -1.74 - 4. 19.00 .95 17.32 .87 -1.68 - 8. m 2.31 .23 2.21 .11 - 8. ium 2.31 .23 2.21 .11 - 10 - 4. lum 13.00 1.30 12.24 .62 76 - 5. 12.00 8.07 .41 93 -10.	roMatter						
n 10.19 1.02 8.44 .43 -1.75 -17.	luminum	17.00	ω	7.1	ω	근	
36.00 1.80 34.26 1.72 -1.74 - 4. 19.00 .95 17.32 .87 -1.68 - 8. ium 2.31 .23 2.21 .1110 - 8. ium 13.00 1.20 12.24 .6276 - 5. 12.00 1.20 8.07 .4193 -10.	ilicon	•	0	8.4	4	1.7	17.
n 19.00 .95 17.32 .87 -1.68 - 8. 12.32 .62 11.22 .56 -1.10 - 8. ium 2.31 .23 2.21 .11 - 10 4. lum 13.00 1.30 12.24 .62 76 - 5. lum 12.00 1.20 12.77 .65 .77 6. 9.00 .90 8.07 .41 93 -10.	opper	9	ω.	4.2	.7	1.7	4
ium 12.32 .62 11.22 .56 -1.10 -8. ssium 2.31 .23 2.21 .1110 - 8. ssium 13.00 1.30 12.24 .6276 - 5. 12.00 1.20 12.77 .65 .77 6. 9.00 .90 8.07 .4193 -10.	ulfur	9	σ	7.3	ω	1.6	ω
ssium 2.3123 2.21 .1110 -4. dium 13.00 1.30 12.24 .6276 -5. 12.00 1.20 12.77 .65 .77 6. 9.00 8.07 .4193 -10.	alcium	2	9	1.2	S	1.1	ω
dium 13.00 1.30 12.24 .62 76 - 5. 12.00 1.20 12.77 .65 .77 6. 9.00 8.07 .41 93 -10.	otassium	•	2	2.2	Н	۲.	4
12.00 1.20 12.77 .65 .77 6. 9.00 .90 8.07 .4193 -10.	anadium	ъ.	٣.	2.2	9	. 7	Ω •
9.00 8.07 .4193 -10.	ron	ς,	2.	2.7	9	7	•
	ead	•	9	8.0	4	6.	10.







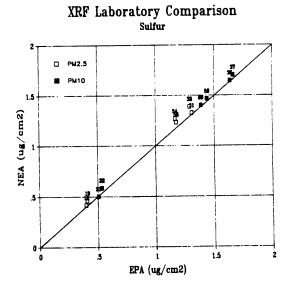
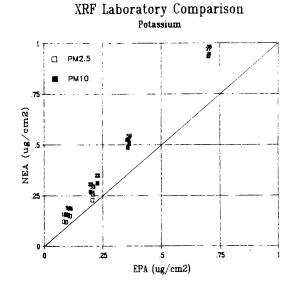
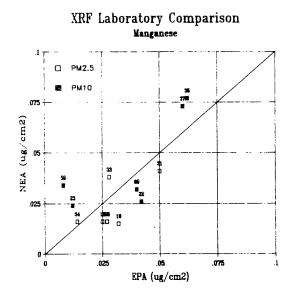


Figure 6-1. Scatter diagram of XRF measurements of silicon, aluminum, iron, and sulfur concentrations by NEA and EPA/NSI.

EPA (ug/cm2)





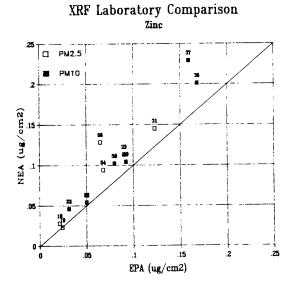


Figure 6-1 (Continued). Scatter diagram of XRF measurements of calcium, potassium, manganese, and zinc concentrations by NEA and EPA/NSI.

Variation Across Filter by PIXE

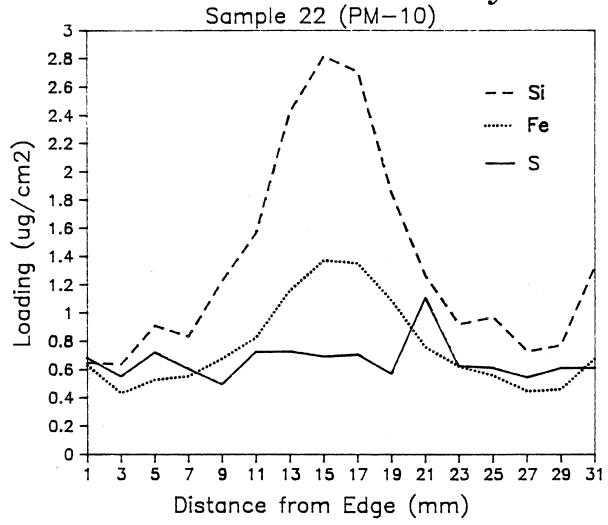


Figure 6-2. PIXE measurement of concentration gradient across the filter by UCD.

TABLE 6-2

Analysis of Iron and Aluminum by XRF and INAA

Element Size, um	Q **	XRF XRF ug/fil	INAA 1.1/62	XRF ug/fil	XRF Lug/fil	XRF Ug/fil	EPA/ UM	EPA/ mean XRF
Aluminum	f 8 1						-	! ! !
<2.5	60	1.01 ± .04	1.15 ± .15	5 1.08 ± .08	1.27 ± .22		80 80	98.
<2.5	E.	1.67 ± .06	1.80 ± .22	1.70 ± .10	2.38 ± .38		6	.82
<2.5	54	1.29 ± .05	2.35 ± .30	9 2.17 ± .10	1.98 ± .32		. 55	. 62
4.00	23	2.76 ± .09	3.40 ± .45	8.25 ± 2.51	3.89 ± .72		6 0	34.
4.00	35	$10.05 \pm .27$	8.90 ± 1.00	3 28.56 ± 8.47	15.81 ± 2.51		1.13	4.
4 1 6	58	5.26 ± .15	5.70 ± .70	0 17.95 ± 5.35	8.64 ± 1.44		. 92	. 40
40.7								
<2.5	0	2.29 ± .12	1.98 ± .28	3 2.34 ± .02	2.67 ± .15	2.37	1.16	ნ .
<2.5	31	4.55 ± .18	3.38 ± .35	5 4.39 ± .03	5.24 ± .27	4.22	1.35	66.
<2.5	54	3.25 ± .15	2.55 ± .33	3.40 ±	4.00 ± .21	3.19	1.28	.92
<10	23	6.94 ± .24	4.90 ± .45	6.40 ± .03		6.57	1.42	1.01
×10	35	18.55 ± .53	12.20 ± .75	20.74 ±	23.87 ± 1.26	20.45	1.52	98.
<10	58	10.97 ± .35	6.90 ± 66.9		13.23 ± .73	10.28	1.59	86.

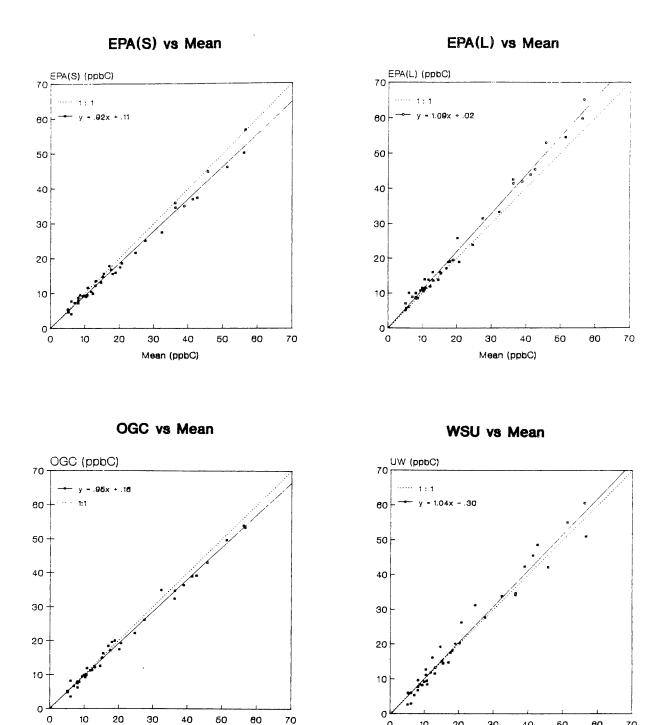
Concentrations are corrected for field blanks. Uncertainties are ± 1 standard deviation.

Additional ongoing activities include comparisons of the XRF data from the SCAQS samples with PIXE data from UCD's DRUM and IMPROVE samplers, which were operated concurrently at several sites, and PIXE scans of a subset of SCAQS samples. The PIXE scans will be used to determine whether it is necessary to adjust the XRF data and whether a constant factor can be used.

6.3.2 Speciated Hydrocarbons

Three ambient air samples were provided by the Oregon Graduate Center (OGC) and were analyzed by GC at EPA's AREAL and at OGC. At EPA, the samples were analyzed by L. Stockburger of the Heterogeneous Chemistry and Aerosol Research Branch [EPA(S)], and by W. Lonneman of the Gas Phase Photochemistry Branch [EPA(L)]. The samples were analyzed a minimum of three times by each laboratory in round-robin fashion over a course of 6 months. samples were also analyzed once at Washington State University. The SCAQS samples were analyzed by EPA(S) for C_4 - C_{10} hydrocarbons and by OGC for C2 and C3 hydrocarbons due to the poor resolution of C, and C, compounds by the EPA(S) system. QA included reanalysis of 60 SCAQS samples by GC/MS and a study of the effect of sample Results of the sample storage study are storage by EPA(S). documented elsewhere (Stockburger 1989). In addition, 10 percent of the SCAQS samples were reanalyzed by OGC and 24 samples were reanalyzed by EPA(L).

Results of the laboratory comparison for speciated hydrocarbon analysis were within acceptable ranges. The scatter diagrams in Figure 6-3 show that the values reported by the SCAQS laboratory, EPA(S), are within 8 percent of the mean of all the laboratories. Figure 6-4 shows that the coefficients of variation among the four laboratories are generally within 10 percent when the concentration is above 5 ppbC. Hydrocarbons with apparent identification problems were deleted from the comparison. Such hydrocarbons accounted for 10 to 15 percent of the total concentration. The most common problem was the varying ability among the laboratories



Scatter diagram of hydrocarbon concentrations Figure 6-3. (> 5 ppbC) measured by each laboratory versus the mean.

Mean (ppbC)

50

40

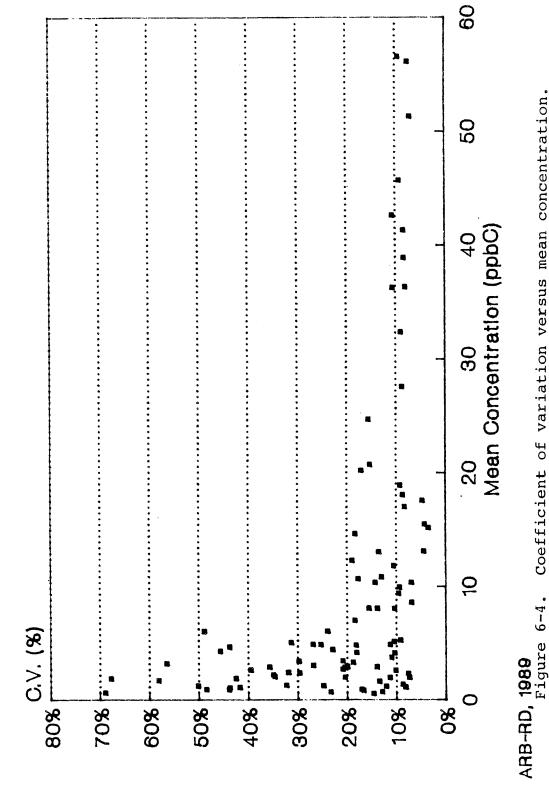
30

Mean (ppbC)

60

70

Coef. of Variation vs Mean Concentration SCAQS Hydrocarbon Comparison Study



Coefficient of variation versus mean concentration.

to resolve closely spaced peaks in the chromatogram. The percentage of the total concentration of hydrocarbons identified and the coefficients of variation for individual and various sums (includes all data) by functional groups are given in Table 6-3.

The data originally reported by OGC in units of ppbC were adjusted by a factor of 1.13. The adjustment was made to normalize the ug/m³ to ppbC conversion to propane.

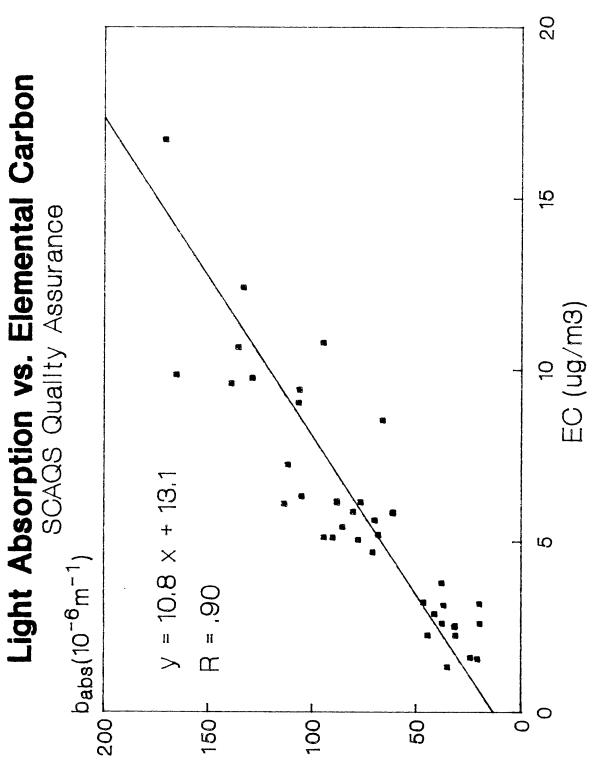
6.3.3 Light Absorption

Optical extinction by absorption (babs) was measured on the SCAQS polycarbonate filters by Radiance Research using the Integrating Plate Method (IPM). The filters were originally analyzed at UCD by IPM. Uncertainties in the UCD data were high due to the lack of prior tare measurements and excessive variability in the transmittance of blank filters. Radiance Research was able to improve the accuracy of the measurement by using the unsampled edge of each filter to make the unsampled tare. Most of the filters contained what appeared to be oil spots. Transmittance was measured within areas unaffected by the spots. Light absorption data for 40 SCAQS samples were correlated against concentrations of elemental carbon reported by ENSR for the corresponding time periods.

A scatter diagram of b_{abs} measured by Radiance Research versus elemental carbon concentration measured by ENSR is shown in Figure 6-5. A factor of 0.8 has been applied to b_{abs} data to correct for the positive artifact associated with the use of Nuclepore filters. The resulting correlation coefficient (0.9) and absorption coefficient per unit mass (10.8 m^2/g) are very reasonable.

TABLE 6-3
SCAQS HYDROCARBON COMPARISON STUDY

C ₄ - C ₉ Hydrocarbons	Sample 108	Sample 109	Sample 146
Coefficient of Variation (%) Individual HCs > 5 ppbC	10.6 ± 4.9	9.9 ± 3.7	11.2 ± 5.1
Total Paraffins	11.6	13.2	9.6
Total Olefins	32.3	22.8	50.6
Total Aromatics	13.6	5.8	12.3
Total Identified	11.2	8.0	10.0
Total (Including Unknowns)	9.7	8.1	9.3
Mean % Identified	86.2	89.7	85.4



Scatter diagram of light absorption measured by Radiance Research versus elemental carbon concentrations measured by ENSR. Figure 6-5.

6.3.4 Peroxyacetyl Nitrate

Several informal measurement comparisons were arranged by DGA, Inc. (DGA) during the summer field study. Measurements of the diluted outputs of the DGA PAN generator by DGA (EC-GC) were compared separately with side-by-side measurements made by General Motors Research Laboratory (EC-GC), University of Denver (Luminol-GC), and EPA (EC-GC). Ambient measurements of PAN during the summer field study by DGA, UCD, and EPA were also compared. Side-by-side measurements of the PAN generator outputs were made during the fall study by DGA and Unisearch Associates, Inc (Luminol-GC). A comparison of calibration methods was conducted at EPA in Research Triangle Park, North Carolina in September 1988 to resolve the difference between the ambient PAN measurements by EPA and DGA.

The time-series plot in Figure 6-6 of ambient measurement of PAN by DGA and EPA shows good correlation (i.e. good precision) but a consistently large bias (i.e. poor accuracy). The relative difference as a function of concentration is shown in Figure 6-7. The mean relative difference for concentrations above 5 ppb is 28.3 ± 11.6 percent. A comparison of the alkaline hydrolysis method of calibration used by DGA and the FTIR method used by EPA showed no significant difference between methods. DGA reports a relative measurement uncertainty of 11 to 50 percent with typical values in the range of 13 to 18 percent. Results of the comparison studies for PAN are documented in a report prepared by Daniel Grosjean Associates (1989).

PAN Measurements, DGA vs EPA Claremont, August 27-29, 1987

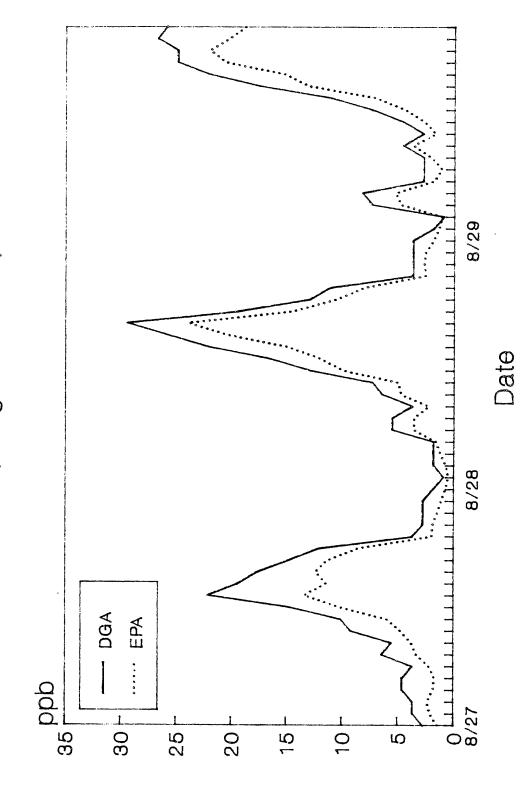
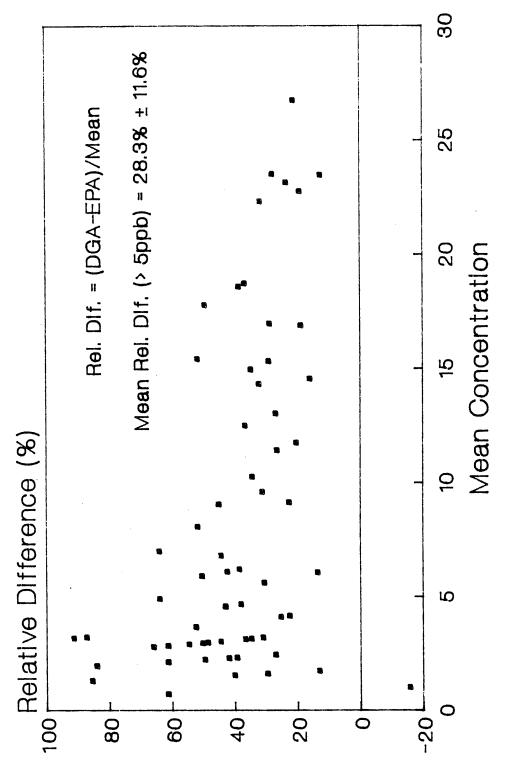


Figure 6-6. Ambient measurement of PAN by DGA and by EPA during SCAQS.

Peroxyacetyl Nitrate, DGA vs EPA SCAQS, Claremont



by DGA and by EPA Relative difference of PAN measurements versus mean concentration. Figure 6-7.

7. MEASUREMENT ACCURACY AND PRECISION

The SCAQS Data Archive includes a field for measurement uncertainty to accompany each data value. Each participant who submits data, also submits an estimate of uncertainty with his or her data. The uncertainty field may represent precision or a combination of accuracy and precision, depending on how the uncertainty was determined. ENSR reviews the basis for measurement uncertainty in conjunction with the measurement specific managers, compares this with QA audit or intercomparison results when possible, and compiles an assessment of measurement accuracy and precision for each measurement.

Most uncertainties determined through internal QC checks (i.e., checks applied by the participant while collecting data), such as replicate sampling, frequent calibration checks, or x-ray counting statistics, generate measures of precision. Manufacturer's specifications, e.g., for meteorological instrumentation, often report accuracy and precision. However, these should be considered precisions by the data base user. Accuracy is usually affected by errors involving improper calibration or operation that result in inaccurate data (e.g., a wind direction sensor not accurately aligned with true north).

External QA checks such as system and performance audits provide accuracy checks for the components of a measurement. For example, flow rate audits and chemistry laboratory audits can confirm the accuracy of sample volume and filter concentration determinations for the SCAQS sampler. Assumptions regarding transport of particles and gases through the sampler to the filter, filter collection efficiency, filter artifacts, sample handling, etc. remain untested. System audits review assumptions and procedures, and attempt to verify that well characterized, accurate procedures are being used.

External QA checks such as intercomparisons among different methods provide accuracy checks for an overall measurement. For example, the integrating plate method for measuring the light absorption of an aerosol collected on a filter, is known to overestimate the aerosol's atmospheric absorption coefficient. A correction factor is applied, but the factor is not known accurately. Comparison of the integrating plate method with measurements of elemental carbon, or with absorption coefficient determined through teleradiometry, provides a check on accuracy of the final measurement without checking component measurements or assumptions.

Additional verification of data accuracy is provided by the data This process will be described in detail in validation process. ENSR's final report to the ARB on SCAQS Data Management. In brief, the validation process screens measurements for unusual behavior such as outliers or sharp temporal spikes, checks for consistency among different methods and measurements of similar species, and checks for physical consistency in the relationships among measurements of different species. The validation is performed in three phases: by the participants, before data are submitted to the data manager; by the data management team in conjunction with the participants, after data are received by the data manager; and finally, by users of the data, after data have been released to the The data validation process produces two scientific community. results: first, problems are identified, documented, and corrected where feasible, thus improving the quality of data in the archive; second, the results of data validation tests are incorporated as flags and comments in the Archive, thus enhancing the usability of the Archive.

The early stages of data validation, including validation performed by the participants and screening of univariate data displays, are being performed now. Formal collections of validation tests are being compiled for each measurement, and will be applied during the second and third quarters of 1989. As researchers use data during the coming years, it is inevitable that new problems will arise, and the SCAQS Data Archive will need further updates. The mechanism is in place now to document the identification and resolution of future data problems, and any resulting modifications to the archive. Thus, QA will continue to be an integral part of the SCAQS program for years to come.

The issues affecting accuracy and precision are as diverse as the SCAQS measurements. While the results of external QA audits are generally too few to summarize quantitative, they are statistically, and are not available for all measurements. Further, accuracy data and accuracy questions usually apply to an entire measurement set, whereas it is often appropriate calculate precisions for individual data values using propagation Thus, uncertainties in the SCAQS Data Archive depend of errors. primarily on internal QC data and primarily represent precision.

Estimates of lower detection limits, precisions, and accuracies for each SCAQS measurement have been compiled in Table 7-1. This table includes a discussion of those issues known to affect accuracy that are difficult to quantify. The discussions also compare audit and intercomparison results with accuracies and precisions reported by the participants.

TABLE 7-1

UNCERTAINTY FOR SCAQS MEASUREMENTS

	Comments	Positive bias due to: 1. Partial retention of NO2 on collection media. 2. Formation of HONO on sampler inlet and other surfaces. 3. Hydrolysis of PAN.	
	Location Season LDL Precision Accuracy Audit/Comparison Comments		
	Accuracy		
cid	Precision	+/- 10%	+/- 15%
urement Catagory: Nitrous Acid	101	Summer 0.6 ppb	LARE LBCC Summer 0.6 ppb
tagory:	Season	Surmer Fall	Summer Fall
Measurement Ca	Location	30 8 T	CLARE LBCC LBCC
¥	Method	Annular denuders counted with Na2CO3-glycerine and analysis of NO2 by IC	DOAS
	ā	Appel	Winer
	Group	AIHL	UCR
	Darameter(s) Group	HONO	HONO

	Comments	1. Positive bias from 03 neg. interf. reaction with SO2->HMSA 2. Line loss of 7% to 40% 3. CE's values near one order magnitude higher than Unisearch TDLAS data	
	Location Season LDL Precision Accuracy Audit/Comparison Comments		
	Accuracy		
	Precision	0-1 +/-40 1-2 +/-7x <2 +/-4x	+/- 10%
200	101	0.5 pdb	Summer 0.5 ppbv +/- 10%
	Season	Sumer	Summer Fall
	Location	CLARE,DOLA Summer 0.5 ppb 0-1 +/-40 LBCC, RUB 1-2 +/-7x <2 +/-4x	CLARE
	Method	Brookhaven Impinger using peroxide catalyzed p-hydroxyphenylacetic acid fluorescense tech. NO to remove 03, HCHO, SO2	TDLAS
	ī	Brookhaven	Mckay
	Group	30	Unisrch
	Darameter(s)	H202	H202

TABLE 7-1 CONTINUED UNCERTAINTY FOR SCAQS MEASUREMENTS

PI Appel Horrocks Knapp Anderson/ Hegg		Measurement of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of t	Season Summer Fall Summer Fall Fall Buth		ic Acid Precision Accur +/- 10% Per data +/- 10% per data	acy Audit/Comparison	Comments Precision from side-by-side test of ten samplers by AV
Group AIHL ARB CE/AV EPA STI/UM	Appel Horrocks Knapp Anderson/	Appel Annular Denuder coated with Na2CO3-glycerol Horrocks Denuder Difference SCAQS Sampler Denuder difference Knapp Transition Flow Reactor Anderson/ Aircraft: filter chemistry Hegg	Appel Annular Denuder coated LBG With Na2CO3-glycerol LBG Horrocks Denuder Difference CL/ Knapp Transition Flow Reactor CL/ Anderson/ Aircraft: filter chemistry LBG Hegg	Appel Arrular Deruder coated Location Season with Na2co3-glycerol LBCC Fall Horrocks Deruder Difference CLARE Surmer SCAQS Sampler Deruder 78 & 2A Surmer difference Transition Flow Reactor CLARE, RUB Surmer LBCC Fall Anderson/ Aircraft: filter chemistry Both Hegg	Appel Annular Denuder coated Location Season LDI Horrocks Denuder Difference CLARE Summer 0.1 pg SCAQS Sampler Denuder 78 & 2A Summer 3 pg difference SA & LBCC Fall Knapp Transition Flow Reactor CLARE, RUB Summer 0.9 pg Anderson/ Aircraft: filter chemistry Both 6 ug,	Appel Annular Denuder coated Location Season LDL Location Season LDL Location Season LDL LBCC Summer 0.2 ppb LBCC Fall CLARE Summer 0.1 ppb Gifference CLARE Summer 0.1 ppb Gifference TRB & 2A Summer 3 ppb Gifference SA & LBCC Fall CLARE, RUB Summer 0.9 ppb LBCC LBCC LBCC LBCC LBCC LBCC LBCC LBC	Appel Annular Denuder coated Location Season LDL with Na2c03-glycerol LBCC Summer 0.2 ppb LBCC Fall CLARE Summer 0.1 ppb Gifference CLARE Summer 3 ppb difference Transition Flow Reactor CLARE, RUB Summer 0.9 ppb LBCC Rall Anderson/ Aircraft: filter chemistry Both 6 ug/m³

Parameter(s) Group NH3 AIHL	Group	Appel	Method Annular denuder citric acid-glycerine	Heasurement Catagory: Ammonia/Ammonium Location Season LDL Precisi LBCC Summer .15 ppb +/- 5% Fall Class DCC Fall	Season Surmer Fall		monium Precision +/- 5%	Accuracy	Ammonia/Ammonium LDL Precision Accuracy Audit/Comparison Comments .15 ppb +/- 5% Sampler of loss to accuracy Audit/Comparison Comments	Comments Sampler designed to keep line loss to a minimum.
NH3 Gaseous NH4 PM10 NH4			inorganic ion size distrubutions SCAQS Sampler	RUB DOLA, LBCC Fall 78 & 2A Summ 58 & LBCC Fall	Fall Sumer Fall	Fall 1 ug/m ³	+/- 42%	₹ 2	audit: 5-10% comparison: 3-8%	Precision based on side by side test.
PM2.5 NH4 NH3 Gaseous NH4 PM10 NH4 PM2.5 NH4	STI/UW	Anderson/ Hegg	Aircraft: filter chemistry		Both	NH; 0.6 ωg/m ³ NH3: 2.5 ωg/m ³	per data			

TABLE 7-1 CONTINUED

UNCERTAINTY FOR SCADS MEASUREMENTS

Measurement Catagory: Carbonyls

ts					
Commen					
Accuracy Audit/Comparison Comments					
S AM					
Precision	*/- 10 %	2	1.12 PPB 0.89 PPB 1.32 PPB 0.30 PPB 0.37 PPB 0.37 PPB 0.37 PPB 0.37 PPB 0.37 PPB	+/- 30%	+/-10%
רפד	0.1 90 90	ċ	4.1 0.0 0.0 1.0 1.0 1.0 1.0 0.0 0.0 0.0 0	.3.0 ppbv	0.1 ppbv
Season	Sumer Fall	Surmer	Both	Summer Fall	Summer Fall
Location	78 & 2A 58 & LBCC	DOLA LBCC CLARE	!	LBCC CLARE LBCC	CLARE LBCC
Method	DNPH cartriges and sequential sampler and HPLC.	DNPH Sep-pak & HPLC	Aircraft: for carbonyls	Differential Optical absorbtion spectrometry	Tunable diode laser absorption spectrometry (TAMS-150)
PI	Fung	Lonneman	Wright	Winer	Mckay
Group	ENSR	EPA	ST1/UM/ ENSR	S S	Unisrch
Parameter(s)	Formaldehyde Acetaldehyde Acetone Acrolein Propanol Methylethyl- ketones Butyaldehyde Pentenal	Formaldehyde Acetaldehyde + 20 other carbonyls	L Formaldehyde O Acetaldehyde Acetone Acetone Acrolein Propanal MEK Butanal Pentanal Hexanone Benzaldehyde	Formaldehyde	Formaldehyde

TABLE 7-1 CONTINUED

SCAQS MEASUREMENTS
SCAGS
õ
UNCERTAINTY

HC Speciation

Measurement Catagory:

Parameter(s)	Group	Id	Method	Location	Season		5	Accuracy	Audit/Comparison	Comments
C4 - C12 hydrocarbons	E P A	Knapp & Stockburger	SS cannisters/GC propane standard	78 & 2A 58 & LBCC	Surmer Fall	Mal: .15 ppb MDL: .05	-/- 15%			MQL: Minimum quantifiable limit Interference: any compound that elutes with same retention time responds to FID.
c2 - c12	EPA	Lorneman	Calib. by propane NBS	CLARE, DOLA LBCC	Summer	Mal.: .12 ppb MDl.: .04	+/- 12%			
C2 - C9 hydrocarbons	390	Rassmussen	SS cannisters/GC. Benzene propane & methane primary NBS SRM C2-C10 calibration standard are traceable to the NBS standard through neo-hexane	78 & 2A 58 & LBCC	Sumer	9. dg	C2-C4: 2%	4,0,000		
Hydrocarbons	ST1/UW/ EPA	Knapp	Aircraft: for hydrocarbons	:	Both	٠.	~			
			ă.	Measurement Catagory:	:agory:	PAN				
arameter(s)	Group	Id	Method	Location	Season	רסר	Precision A	Accuracy	Audit/Comparison	Comments
PAN	DGA	Grosjean	PAN by GC, electron capture	78 & 2A ANA, DOLA HAW, LBCC	Surmer Fall	qdd -				
PAN aloft	DGA/STI/ UM	Grosjean	Aircraft: PAN	:	Both	per data	per data			
PAN	EPA	Lonneman/ Ellenson	PAN by GC, electron capture	CLARE	Sumer		~			
PAN	9	Stedman	PAN by GC luminal detector	CLARE	Summer		+/- 10%		·	

UNCERTAINTY FOR SCAQS MEASUREMENTS TABLE 7-1 CONTINUED

Measurement Catagory: Oxides of Nitrogen

Darameter(s)	Group	Id	Method	Location Season	Season	101	Precision	Accuracy	Precision Accuracy Audit/Comparison	Comments
NO NO2 Artifact NO2	AIHL	Appel	Modified TECO 148/E with Na2CO3-glycerol denuder	7800	Fall	~	¢.			
N N N N N N N N N N N N N N N N N N N	АФИ	Воре		ANA, AZUSA DOLA, HAW ANA, DOLA, HAW, RUB	Surmer Fall	.001 ppm	.001 ppm	2-3%	audit: 2-6% for NO2	
NO NO2	ARB	Kowalski	Monitor Labs 8440	2081	Both	mcdd 7,00°.	.001 ppm		audit: 5-10% for NO2	
N02	ARB	وسار	Dasibi 2008	CLARE LBCC	Surmer Fall	¢.	c.			
9 % % 7-	¥	Chan	Monitor Labs 8440	INS	Surmer	.004 ppm	.001 ppm			
XON -8	EPA	Lonneman/ Ellenson	Monitor Labs 8440 with prefilter	CLARE	Surmer	.004 ppm	.001 ppm			
N N N N X X	5	Wolff	Monitor Labs	CLARE	Summer Fall	.004 ppm	×9 -/+		audit: 5-10% for NO2	
N N XON	SCE/AV	Games	Monitor Labs 8440E	Alamitos	Both	.004 ppm	.001 mgd			
N NO NO NO NO NO NO NO NO NO NO NO NO NO N	ST1/UW	Anderson/ Hegg	Aircraft: Filter chemistry	!	Both	.004 ppm	dq f		audit: 10-12% for NO2	
N02		Winer	DOAS	CLARE, LBCC LBCC	Summer	c-	C-			

TABLE 7-1 CONTINUED

	SCAGS MEASUREMENTS
,	FOR
	UNCERTAINTY

Measurement Catagory: Carbon Monxide

Parameter(s)	Group	P.I.	Method	Location ANA, AZUSA	Season	.001 pom	Precision .001 pom	Accuracy 2-3%	Audit/Comparison Comments audit: 5%	Comments
		<u>}</u>		HAW, DOLA, ANA, DOLA, HAW, RUB	Fall	<u> </u>		<u>.</u>		
03	ARB	Kowalski	Dasibi 3003	LBCC	Both	rod mod	L.		audit: 2-6%	
03	8	Chan	Dasibi 3003	SNI	Summer	.1 ppm	mod t.			
ಟ	3	Wolff	Dasibi	CLARE	Summer	ċ	+/- 8.5%		audit: 5-10%	
00	SEC/AV	Games	Dasibi 3003	Alamitos	Both	.1 ppm	mad 1.			
CO aloft	STI	Anderson	Aircraft	:	Both	c.	c		audit: 3%	
			Æ	Measurement Catagory:	agory:	Ozone				
arameter(s)	Group	PI	Method	Location	Season	רסר	Precision	Accuracy	Audit/Comparison Comments	Comments
03	AIHL) Pddy	Dasibi 1003AH	7987	Both	.00 ppm	.001 ppm			
03	AQMD	Bope		ANA, AZUSA HAW, DOLA	Summer	.001 ppm	.001 ppm	2-3%	audit: 5-10%	
				ANA, DOLA, HAW, RUB	Fall					
03	ARB	Kowalski	Dasibi 1003	LBCC	Both	.004 ppm	.001 ppm		audit: 5%	
03 aloft	ARB	Bennett	Aircraft: Dasibi 1003		Summer	.004 ppm	.005 ppm		audit: 5%	
03	۸۷	Chan	Dasibi 1003-AH	SNI	Summer	.004 ppm	.001 ppm			
03	.	Wolff	Dasibi	CLARE LBCC	Surmer Fall	.004 ppm	*/- 6.5%		audit: 5%	
03	3	Wolff	Monitor Labs	CLARE LBCC	Summer Fall	ć	+/- 6.5%		audit: 5%	
03	SEC/AV	Games	Dasibi 1003-АН	Alamitos	Both	.004 ppm	.001 ppm			
03 aloft	STI/UW	Anderson/ Hegg	Aircraft	:	Both	٥.	7 ppb		audit: 5-12%	

TABLE 7-1 CONTINUED UNCERTAINTY FOR SCAQS MEASUREMENTS

			*	Measurement Catagory:	agory:	Wind Speed			
Darameter(c)	Group	Id	Method	Location	Season	101	ક	Accuracy Audit/Comparison	n Comments
SM	AOMD	Bope		ANA, AZUSA HAW, DOLA	Summer	0.5 mph	1.0 mph	****	
				ANA, DOLA, HAW, RUB	Fall				
S.A.	ARB	Kowalski		רפככ	Both	~	.3 m/s		
SH	٩٨	Chan	MRI 1022	SNI	Summer	.223 m/s	s/m 790.	, , , , , , , , , , , , , , , , , , ,	
SM N	3	Wolff	Climatronix	CLARE	Summer Fall	ċ.	~		
SH	SEC/AV	Games	MRI 1022	Alamitos	Both	.223 m/s	s/m 290°		
			Ā	Measurement Catagory:	agory:	Wind Direction	tion		
Darameter(s)	Group	14	Method	Location	Season	101	-	Accuracy Audit/Comparison	n Comments
9 7−1	AGMD	Воре		HAW, DOLA	Summer	WS=.5 mph	2.5 deg.		
0				HAW, RUB				1	
9	ARB	Kowalski		2281	Both	ć			
9	AV	Chan	MRI 1022	SNI	Summer	WS=.3 m/s	2.5 deg.		
on A	₹	Wolff	Climatronx	CLARE LBCC	Summer Fall	~	10 deg		
9	SEC/AV	Games	MRI 1022	Alamitos	Both	WS=.3 m/s 2.5 deg.	2.5 deg.		

TABLE 7-1 CONTINUED UNCERTAINTY FOR SCAQS MEASUREMENTS

3	Group AQHD AV AV GH GH SEC/AV	PI Bope Kowalski Chan Wolff	Method	Heasurement Catagory: Location Season ANA, AZUSA Summer HAW, DOLA ANA, DOLA HAW, RUB LBCC Both SNI Summer CLARE Summer LBCC Fall Alamitos Both Alamitos Both	Summer Fall Summer Summer Fall Both Both	Temperatu LDL N/A N/A N/A N/A N/A N/A N/A N/A N/A	Precision 1 degf 1.15 degC 1.10 degC	Accuracy 2%	Precision Accuracy Audit/Comparison Comments 1 degF 2% 10 degC 15 degC 11 degC 11 degC	Coments
TEMP aloft ST	STI/UW	Anderson/	Aircraft		Both	W/W	.1 degc			
	EC/AV	Games	MRI 1022	Alamitos	Both	N/A	.10 degc			
TEMP10 T1 - T10										
	T	Wolff	Climatronix	CLARE LBCC	Summer Fall	N/A	.15 degC			
		Chan	MRI 1022	SNI	Summer	N/A	.10 degc			
	88	Kowalski		2087	Both	N/A	٠			
				ANA, DOLA, HAW, RUB	Fall					
	£	Воре		ANA, AZUSA HAW, DOLA	Summer		1 degF	స		
Parameter(s)	Group	PI	Method	Location	Season	- 1	Precision	Accuracy	Audit/Comparison	Comments
			₩	easurement Cat	tagory:		ē			

1			Me	Measurement Catagory:	tagory:	Dew Point					
Parameter(s) Group	Group	14	Method	Location Season	Season	101		Accuracy	Precision Accuracy Audit/Companison Comments	Comments	
DUPT	AQMD	Воре		ANA, AZUSA	Summer	N/A	<u> </u>	2%			
				ANA, DOLA,	Fall						
				HAW, RUB							
DWPT	ARB	Kowalski		TBCC	Both	N/A	¢.				
DuPT	₹	Chan	MRI 1022	SNI	Surmer	N/A	0.1 degC				
Tano	35	Wolff	Climatronix	CLARE LBCC	Summer Fall	N/A	0.15 degc				
DWPT	SEC/AV	Games	MRI 1022	Alamitos	Both	N/A	0.1 degc				
DWPT aloft	ST1/UM	Anderson/ Hegg	Aircraft: Filter chemistry	:	Both	N/A	1.0 degC				

TABLE 7-1 CONTINUED UNCERTAINTY FOR SCAOS MEASUREMENTS

	Accuracy Audit/Comparison Comments					
	Audit/Com					
	Precision	per data	lug + 5% per stage	+/- 3.1%	per data	+/- 12%
Carbon	101	OC: 3.6 ug/m ³ EC: 0.2 ug/m ³	OC: 1.0 EC: 0.5 ug/m³ per stage	0.3 ug/m ³ +/- 3.1%	EC: 3.0 ug/m ³ TC: 5.0 ug/m ³	0C: 7.0 ug/m ³ EC: 0.4 ug/m ³
tagory:	Season	Summer Fall	Summer	Summer	Both	Sumer
Measurement Catagory:	Location	78 & 2A Summer 58 & LBCC Fall	CLARE,LBCC RUB DOLA, LBCC	CLARE		CLARE
Ĭ	Method	SCAQS Sampler	MOUDI for sizes: < .032um; .034072um; .07217um; .1728um; .2856um; .56-1um; 1-1.8um; 1.8-3.2	In-situ elemental, organic and total carbon	Aircraft: Filter chemistry carbon aloft	Dichotomous sampler for elemental and organic carbon
	I	Taketomo	McMurry	Huntzicker	Anderson/ Hegg	Main
	Group	ENSR/AV	5	390	STI/UW	UCLA-2
	Darameter(s)	PM10 EC PM2.5 EC PM10 OC PM2.5 OC	EC all cuts OC all cuts	in-situ EC in-situ OC in-situ TC	PM10 EC PM2.5 EC PM10 OC PM2.5 OC	PM10 EC PM10 RC PM2.5 EC PM2.5 RC

Deremeter(s) Groun	3	14	Method	Location Season	Season	TOT	Precision	Accuracy	LDL Precision Accuracy Audit/Comparison Comments	Comments
Bsp	AGMD	Воре	MRI 1560	ANA, AZUSA HAW, DOLA ANA, DOLA, HAW, RUB		3E-5/m	10%			LDL from manual - zero drift indicated on calibration sheets.
Bsp	₹	Chan	MRI 1560	CLARE, LBCC RUB, SNI LBCC	Summer	3E-5/m	10%			
Bsp	3	Wolff	Modified MRI 1550	CLARE LBCC	Summer Fall	3E-6/m	ř			
Bsp aloft	ST1/UM	Anderson/ Hegg	Aircraft: MRI 1569		Both	3E-6/m	m/ ₉₋ 01 -/+			
Bsp	'n	Rood	Nephelometer	CLARE, RUB Summer 3E-6/m	Summer	3E-6/m	7%	2%		

8sp

Measurement Catagory:

TABLE 7-1 CONTINUED UNCERTAINTY FOR SCAQS MEASUREMENTS

	Comments		Participants should call Dr. Hansen about precision.	Filter absorption over estimates aerosol Babs by ~20%		·			Comments		
	Accuracy Audit/Comparison Comments								Audit/Comparison		
	Accuracy		2%						Accuracy		
	Precision	5E-6/m	Max of 20% and 5E-6/m	per data	per data	per data	2%		Precision	per data	per data
Babs	רטר	3E-6/m	m/9-39	8E-6/m	10 ⁻⁶ /m	per data	¢.	Bext	101	20/Mm	¢.
tagory:	Season	Summer	Summer	Summer	Both	Summer Fall	Summer Fall	tagory:	Season	Summer	Summer Fall
Measurement Catagory:	Location	CLARE	CLARE	78 & 2A 58 & LBCC	;	CLARE, LBCC RUB DOLA, LBCC	CLARE	Measurement Catagory:	Location	CLARE	CLARE LBCC
¥	Method	Spectrophone	Aethelometer 2 size cuts:	SCAQS Sampler	Aircraft: Filter chemistry	IMPROVE teflon filter	Nuclepore filter	Æ	Method	Teleradiometer	Telephotometer for 10 wavelengths
	Iď	Adams	Hansen	Weiss	Weiss/ Anderson/ Head	Matsumura	Hitzen- berger		14	Richards	Hitzen- berger
	Group	Ford	181	RR/AV	RR/STI/ UN	99	U.Vienna		Group	STI	U.Vienna
	Parameter(s)	Babs	Babs	Babs	Babs aloft	Babs	Babs	7-1	S Parameter(s)	Bext	Bext

Parameter(s) Group	Group	PI	Method	Location Season	Season		Precision	Accuracy	LDL Precision Accuracy Audit/Comparison Comments	Corments
	;	3			5					
			2	**************************************	6	4	0 + 0 10 10 10 10 10 10 10 10 10 10 10 10 1			
			Ĕ	שפמסתו פוופנור בפרמאסו ץ:	agol y:	חוו אוחור	er kadiation			
Parameter(s)	Group	PI	Method	Location Season	Season	LDL	Precision	Accuracy	LDL Precision Accuracy Audit/Comparison	Comments
ΛΩ	ARB	Kowalski	Epply UV photometer	æ	Summer	W/A	7 ly/min			
A)	٩	Chan	Epply UV photometer	E,LBCC	Summer	N/A	7 ly/min			
				DOLA, LBCC	Fall					
۸٦	35	Wolff	Epply	CLARE	Summer	N/A	7 ty/min			

Measurement Catagory: Path Radiance

TABLE 7-1 CONTINUED

UNCERTAINTY FOR SCAQS MEASUREMENTS

Solar Radiation
Catagory:
Measurement

Deremeter(c)	Group		Method	Location	Season	TOT	Precision	Accuracy	Precision Accuracy Audit/Comparison Comments	Comments
	3	Wolff	Ерріу	CLARE LBCC	Summer Fall	N/A	7 ly/min			
	_					•	:			
			·	Measurement Catagory:	agory:	Relative Mumidity	umidity			
r(s)	Group	Id	Method	Location	Season	LOL	Precision	Accuracy	Audit/Comparison	Comments
RH	3	Wolff	Climatronix	CLARE LBCC	Summer Fall	c.	*			
			# #	Measurement Catagory:	agory:	Sulfur Dioxide	x i de			
(s)	Group	14	Method	Location	Season	רטר	Precision Accuracy	Accuracy	Audit/Comparison	Comments
S02	ARB	Kowalski	TECO 43	2087	Both	į	i		audit: 28%	
	CE/AV	Countess	SCAOS Sampler	78 & 2A 58 & LBCC	Summer Fall	.1 ug/m3	per data			
	SEC/AV	Games	Meloy 285E	Alami tos	Both	1% full scale	1% full scale			
SO2 aloft	STI	Anderson	Aircraft: Filter chemistry	:	Both	0.6 ug/m³	1.0 ppb		audit: 3%	
			¥.	Measurement Catagory:	agory:	Sulfate				
Darameter(s)	Group	- -	Method	Location	Season	רסר "ן	Precision	Accuracy	Audit/Comparison	Comments
SO4 all size fractions	AIHL	John	Berner Impactor for inorganic ion size distrubutions	CLARE, LBCC RUB DOLA, LBCC	Summer Fall	.06 ug/m²	+/- 3%	× ×		
PM2.5 SO4	ARB	Horrocks	Denuder Difference	CLARE	Summer	-07 ωg/m ³	per data			
PM10 SO4	AV/AQMD	Eden	Anderson SSI HiVol	78 & 2A 58 & LBCC	Summer Fall	0.1 ug/m³	.04 ug/m³			
PM10 SO4 PM2.5 SO4	CE/AV	Countess	SCAQS Sampler	78 & 2A 58 & LBCC	Summer Fall	.04 ug/m³	per data		audit: 5-10% comp.: 5-10%	
TOTAL SO4	EPA	Knapp	TFRs for inorganics	CLARE LBCC	Summer Fall	.07 ug/m³	ž! -/-			
PM10 SO4 PM2.5 SO4	ST1/UN	Anderson/ Hegg	Aircraft: Filter chemistry SO4 aloft		Both	0.6 ug/m³	per data			
PM10 SO4 PM2.5 SO4	UCLA-2	Main	Dichotomous Sampler Teflon filter with Nylasorb backup filter	CLARE	Sumer	.1 ug/ filter	+/- 10%			

TABLE 7-1 CONTINUED UNCERTAINTY FOR SCAQS MEASUREMENTS

Measurement Catagory: Nitrate

Parameter(s)	Parameter(s) Group	ā		Location		101	Precision	Accuracy	LDL Precision Accuracy Audit/Comparison Comments	Comments
AIH	<u>.</u>	r for	Berner Impactor for inorganic ion size	CLARE, LBCC RUB	Summer	.06 ug/m²	+/- 3%	۲ ۲		
			distrubutions	DOLA, LBCC	Fall					
₹	ARB	Horrocks	Denuder Difference	CLARE	Summer	0.5 ug/m³ +/- 10%	*/- 10%			
≪	AV/AGMD	Eden	Anderson SSI HiVol	78 & 2A 58 & LBCC	Summer Fall	0.1 ug/m³	0.1 ug/m³ .05 ug/m³			
0	CE/AV	Countess	SCAQS Sampler	78 & 2A 58 & LBCC	Summer	2.0 ug/m³ per data	per data		audit: 3-8% comparison: 3-8%	
ш	EPA	Knapp	TFRs for inorganics	CLARE	Summer Fall	5.0 ug/m ³ +/- 10%	+/- 10%			
S	STI/UH	Anderson/ Hegg	Aircraft: Filter chemistry NO3 aloft	İ	Both	0.6 ug/m³ per data	per data			
۔	UCLA-2	Wain	Dichotomous Sampler Teflon filter with Nylasorb backup filter	CLARE	Summer	0.3 ωg/m ³ 10%	¥0.			

LDL _ Precision Accuracy Audit/Comparison Comments			
acy Audit/Comp			
ecision Accur	5 ug/m3	r data	r data
רסר "ן אני	Summer 0.1 ug/m² .05 ug/m³ Fali	Summer 0.5 ug/m³ per data	0.6 ug/m³ per data
Season	Summer Fali	Summer Fall	Both
Location Season	78 & 2A 58 & LBCC	78 & 2A 58 & LBCC	:
Method	Anderson SSI HiVol	SCAQS Sampler	Aircraft: Filter chemistry Cl aloft
PI	Eden	Countess	Anderson/ Hegg
Group	AV/AQMD	CE/AV	STI/UN
Parameter(s)	PH10 Cl AV/AGMD Eden	PM10 CL PM2.5 CL	PM10 CL PM2.5 CL

Measurement Catagory: Chloride

TABLE 7-1 CONTINUED

UNCERTAINTY FOR SCAQS MEASUREMENTS

Measurement Catagory: Mass

וסו"	5 ug/m² .05 ug/m³	12 ug/m³ per data	3 +/- 10%	5 ug/m³ per data	8 ug/m³ 10%
Location Season	78 & 2A Summer 58 & LBCC Fall	78 & 2A Summer 58 & LBCC Fall	CLARE Summer	Both	CLARE Summer
Method	_	SCAQS Sampler 7	Rotary impactor, four size C cuts	Aircraft: Filter chemistry Mass aloft	Dichotomous Sampler Teflon filter with
14	Eden	Countess	Noll	Anderson/ Hegg	Main
group.	AV/AGMD	CE/AV	=	STI/UM	UCLA-2
December(s) Group	PM10 Mass	PM10 Mass PM2.5 Mass	Mass	PM10 Mass PM2.5 Mass	PM10 Mass PM2.5 Mass

Measurement Catagory: Sodium

Comments		
Accuracy Audit/Comparison Comments		
Accuracy	8-10%	
Precision	3% 2%	ر per data
רסר	.06ug/m3	1 ug/m³
Season	Summer Fall	Summer Fall
Location	CLARE, LBCC Summer RUB DOLA, LBCC Fall	78 & 2A 58 & LBCC
Method	Berner Impactor for inorganic ion size distrubutions	SCAQS Sampler
ā	John	Countess
group	AIHL	CE/AV
- Parameter(s)	9 Na all cuts AIHL	PM10 Na

Measurement Catagory: Particle Size Distributions

Comments	OPC: .5-7um optical size rumber distribution	PRB: .1-3um optical size number distribution	EAA: .00656um electrical mobility	DMA: .00315um electrical mobility	number distribution
Audit/Comparison					
Accuracy					
Precision	+- 5%			ż	
101	V / N			N/A	
Season	Summer	Fall		Summer	Fall
Location	CLARE, LBCC	DOLA, LBCC		CLARE, LBCC	DOLA, LBCC
Method Location Season LDL Precision Accuracy Audit/Comparison Comments	Climet 208, PMS LASX Probe			Univ. Vienna Diff. Mobility CLARE, LBCC Summer N/A	Analyzer
PI	Moon			Reischl	
Group	N/			U.Vienna Reischl	
Parameter(s) Group	O-0-0	EAA B		DMA	

TABLE 7-1 CONTINUED

CARLEST COACO COL CARLANTELLOS

2
7
w
X
w
9
ಪ
₹
MEASU
'n
2
ب
쫉
0
<u>.</u>
_
≽
-
=
-
7
ü
\overline{c}
3
\supset

Measurement Catagory: XRF/DRUM/IMPROVE

Comments	See Section 6.3.1				
-	per data +/- 15% See Sect. 6.3.1				
Accuracy	+/- 15%				
Precision	per data	per data	per data	per data	per data
רסה	1 ug/cm2	.0107 ug/m³	per data	per data	.4 ug/cm
Season	Summer Fall	Both	Summer Fall	Summer	Sumer
Location	78 & 2A 58 & LBCC	A lami tos	CLARE, LBCC RUB DOLA, LBCC	CLARE, LBCC RUB DOLA, LBCC	CLARE
Method	SCAGS Sampler XRF	XRF by NEA	IMPROVE teflon filters for PM2.5 by PIXE	DRUM by PIXE for size cuts <.069um; .069um24um; .24um34um; .34um56um; .56um-1.15um; 1.15-2.12um 2.12um-4.26um; 4.26-8.54um 8.54um-15um	XRF dichots
<u>.</u>	Knapp	Games	Matsumura	Matsumura	π c
Group	EPA/AV	SCE/AV	9	g	ncLA-2
Parameter(s)	PM10 XRF PM2.5 XRF	PM10, PM2.5 Ag Al As Ba Br Ca Cd Cl Cr Cu Fe Ga Hg In K La Mn Mo Na Ni P Pb Pd Rb S Sb Se Si Sn Sr Ti V Y Zn Zr Mass	PM2.5 Al As Br Ca Cr Cu Fe K Ma Mn Ni Pb S Se Si Ti	Ca Cl Fe K S Zn	PM10, PM2.5 Ag Al As Ba Br Ca Cd Cl Cr Cu Fe Ga Hg In K La Mn Mo Ni P Pb Pd S Se Si Sn Sr Ti V Y Zn Zr

8. REFERENCES

- Chow, J. 1988. Desert Research Institute, Reno, NV, private communication.
- Fitz, D. and J. Zwicker 1988. <u>Design and Testing of the SCAQS Sampler for the SCAQS Study, 1987</u>, AeroVironment Report AV-R-87/649, Monrovia, California (Final Report), California Air Resources Board, Sacramento, California, Contract A6-077-32.
- Hegg, Dean and Peter Hobbs 1988. <u>Cloud and Precipitation</u>
 <u>Scavenging Processes in the South Coast Air Basin</u>, University
 of Washington, ARB Contract No. A4-143-32.
- Hering, S.V. Comparison of Sampling Methods for Carbonaceous Aerosols in Ambient Air, University of California, Los Angeles, Final Report, ART Contract No. A5-154-32, (1988).
- Kellogg, B. 1989. NSI Technology Services Corporation, Research Triangle Park, North Carolina, private communication.
- Lawson, D.R. 1988. <u>Atmos. Environ.</u>, <u>22</u>, additional papers from the NSMCS can be found in <u>Atmos. Environ.</u>, Vol. 22, No. 8, pp. (1988).
- Lawson, D.R. 1989a. Private communication.
- Lawson, D.R., et al. 1989b. Aerosol Science and Technology, in press.
- Lawson, D.R. 1989c. Private communication.
- Stockburger L., K.T. Knapp, and T.G. Ellestad 1989. "Overview and Analysis of SCAQS Hydrocarbon Samples", <u>Presented at the 82nd Annual Meeting of Air and Waste Management Association</u>, Anaheim, California, June, 1989, Paper No. 89-139.1.
- Williams, Edwin L. II, D. Grosjean, Daniel Grosjean and Associates, Inc. 1989. <u>Southern California Air Quality Study:</u>

 <u>Peroxyacetyl Nitrate (PAN) Measurements</u> (Final Report), California Air Resources Board, Sacramento, California, Contract A6-099-32.

9. GLOSSARY

ARB California Air Resources Board

AV AeroVironment

b_{abs} particle light absorption coefficient

CAS Chemical Abstract Service

C-E Combustion Engineering: C-E Environmental, Inc

Camarillo, California

CRC Coordinating Research Council

CSI Columbia Scientific, Inc.

CSMCS Carbonaceous Species Methods Comparison Study

DGA DGA, Inc.

DNPH dinitrophenolhydrazine

DOAS differential optical absorption spectroscopy

DOE Department of Energy

DRI Desert Research Institute

DRUM Davis rotating-drum universal-size-cut monitoring-

sampler

EAA electrical aerosol analyzer

EMSI Environmental Monitoring and Services, Inc.

ENSR Consulting and Engineering, Camarillo, California

EPA AREAL Environmental Protection Agency, Atmospheric Research

and Exposure Assessment Laboratory, Research Triangle

Park, North Carolina

EPA/NSI Northrop Services Inc, under contract to EPA AREAL

EPA(L) Gas Phase Photochemistry Branch

EPA(S) Heterogenous Chemistry and Aerosol Research Branch

FTIR Fourier transform infrared

GC gas chromatography

GC-MS gas chromatography with mass spectrometry

GM General Motors Research Laboratories, Warren, Michigan

HC hydrocarbon

INAA Instrumental Neutron Activation Analysis

IPM integrating plate method

LIDAR light detecting and ranging

MOUDI micro orifice uniform deposit impactor

MSM Measurement Specific Manager. SCAQS measurements have been broken into a number of measurement areas and a MSM has been assigned to oversee the consistency and quality of data within each measurement area.

NASN National Air Surveillance Network

NEA NEA, Inc., Beaverton, Oregon

NSI NSI Technology Services Corporation

NSMCS Nitrogen Species Methods Comparison Study

OGC Oregon Graduate Center

OPC optical particle counter

PAN peroxyacetyl nitrate

PIXE particle-induced x-ray emission

QA Quality Assurance. Reviews and audits by external personnel to verify that measurement methods and QC procedures are adequate to achieve desired results, to verify that these procedures are being followed, and to test whether the desired representativeness, accuracy and precision is achieved in practice.

QC Quality Control. Documentation and procedures to control and verify the representativeness, accuracy and precision of measurement data. These procedures are applied by the group performing the measurements.

SoCAB South Coast Air Basin

SCAQMD South Coast Air Quality Management District

SCAOS Southern California Air Quality Study

SSI size-selective inlet

SOP standard operating procedure

STI Sonoma Technology, Inc.

TDLAS tunable diode laser absorption spectrometer

THC total hydrocarbons

TSD Technical Services Division

UCD University of California, Davis

UW University of Washington

XRF x-ray fluorescence